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COLLABORATIVE STUDY OF PARTICULATE EMISSIONS MEASUREMENTS BY EPA METHODS 2, 3, AND 5 USING PAIRED PARTICULATE SAMPLING TRAINS (MUNICIPAL INCINERATORS)

SOUTHWEST RESEARCH INSTITUTE

PREPARED FOR
ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY

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COLLABORATIVE STUDY OF PARTICULATE EMISSIONS MEASUREMENTS BY EPA METHODS 2, 3, AND 5 USING PAIRED PARTICULATE SAMPLING TRAINS (Municipal Incinerators)

Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

This report represents the results of statistical analyses of data from a collaborative test using paired particulate sampling trains. The purposes of the test were to estimate the minimum variability that can be expected with the use of Method 5 and to determine the effect of spatial/temporal changes in the gas flow on a Method 5 result. The paired train consists of two mirror-image Method 5 trains in a single box, and allows two independent laboratories to obtain simultaneous particulate concentration data with probe nozzles only 5.8 cm apart. The report deals with Method 5, and also Method 2 (Velocity) and Method 3 (Stack Gas Analysis), which are called for in the use of Method 5. In addition, the particulate concentrations are converted to the applicable compliance test result for the source tested, and these are also analyzed. The latest in-house revisions of the EPA methods were used in this test, and the results contained here are applicable to these revisions.

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SUMMARY AND CONCLUSIONS

This report presents the results of statistical analyses of data from a collaborative test using paired particulate sampling trains. The purposes of the test were to estimate the minimum variability that can be expected with the use of EPA Method 5 and to determine any noticeable effect in the particulate concentrations due to spatial/temporal changes in the gas flow at this test site. The paired train consists of two mirror-image Method 5 trains in a single box, and allows two independent laboratories to obtain simultaneous particulate concentration data with probe nozzles only 5.8 cm apart. This report deals with Method 5, and also Method 2 (Velocity) and Method 3 (Stack Gas Analysis) which are called for in the use of Method 5. In addition, the particulate concentrations are converted to the applicable compliance test standard for the source tested, and these are also analyzed. The latest in-house revisions of the EPA methods were used in this test, and the results contained here are applicable to these revisions.

The collaborative test was conducted at a municipal incinerator in Dade County, Florida. Four paired particulate sampling trains were used in the test, and eight concentration determinations were made in each run. Of these, 6 were made by laboratories operating on one side of a paired train, while the other 2 were made by a single laboratory operating the paired train by themselves. There were 13 sampling runs made over a three-week period, with 3 runs the first week and 5 each of the remaining two weeks. The paired-train laboratory was changed each week so that a total of 9 laboratories participated and a total of 104 concentration determinations were made. One of these determinations had to be deleted from the data set due to a broken probe liner and contaminated filter but was replaced with a substituted value for the statistical analysis of the results.

For each factor of interest in the report, precision components are estimated in terms of within-laboratory, laboratory bias and between-laboratory standard deviations and coefficients of variation. These precision estimates pertain to the determination of a single run result and not to the average of three results that is specified in the performance test for compliance section of the *Federal Register*. The results are summarized below.

Method 5–The determined particulate concentration ranged from 81.7 to 254.5 mg/scm. The within-laboratory term is estimated using the differences between determinations by the paired-train laboratory on a given run. The standard deviation estimated using all three laboratories' data is 13.81 mg/scm, or 10.4% of the average determined concentration with 13 degrees of freedom. The laboratory bias standard deviation is estimated from an Analysis of Variance (ANOVA) of the data from the six single-train laboratories. The estimated value is 8.15 mg/scm, or 6.1% of the average determination with 3 degrees of freedom. Combining these two estimates gives a between-laboratory standard deviation of 16.04 mg/scm, or 12.1% of the mean value.

Method 2–The determined velocities ranged from 13.6 to 16.5 m/sec. Only data from the six single-train laboratories are used in this analysis. The precision estimates are obtained using a coefficient of variation approach, where the standard deviations are expressed as a percentage of an unknown mean. The within-laboratory standard deviation is estimated to be 2.2% of the mean value, with 66 degrees of freedom. The between-laboratory standard deviation is estimated as 4.3% of the mean with 5 df. This gives an estimated laboratory bias standard deviation of 3.7% of the mean.

Method 3–There were 7 gas analyses performed on all but the first 4 runs. The paired-train laboratory took one sample for both trains, while one laboratory did not take Orsats during the first four runs. There were 87 determinations of percent carbon dioxide, percent oxygen and dry gas molecular weight, and one substituted value was used to complete the data set. Precision estimates were obtained using an ANOVA approach and are summarized in terms of standard deviations.

- *%CO_2*–The determined concentrations ranged from 1.8 to 3.1 percent CO_2. The within-laboratory standard deviation is estimated to be 0.20 percent CO_2 with 67 degrees of freedom. The

estimated laboratory bias standard deviation is 0.35 percent CO_2, with 6 degrees of freedom. This results in an estimated between-laboratory standard deviation of 0.40 percent CO_2. In terms of relative variation, the between-laboratory coefficient of variation is 16.7% of the mean determined value.

- *$\%O_2$* The determined oxygen concentration ranged from 16.5 to 19.5 percent O_2. The within-laboratory standard deviation is estimated as 0.32 percent O_2 with 67 degrees of freedom. The estimated laboratory bias standard deviation is 0.52 percent O_2 with 6 degrees of freedom. These give a between-laboratory standard deviation estimate of 0.61 percent O_2. No coefficient of variation is expressed for these data since the variation in the O_2 is considered to be more related to the variation in the CO_2 determination than to the actual oxygen level in the stack gas.

- *Dry Gas Molecular Weight* The dry gas molecular weights determined ranged from 28.06 to 29.21 gm/gm-mole. The estimated within-laboratory standard deviation is 0.035 gm/gm-mole with 67 degrees of freedom. The laboratory bias standard deviation estimate is 0.033 gm/gm-mole with 6 degrees of freedom. This gives an estimated between-laboratory standard deviation of 0.048 gm/gm-mole. The variation in this determination is related to the variation in the CO_2 and O_2 determinations rather than the true stack gas molecular weight.

Moisture Fraction The determined moisture fraction ranged from 0.117 to 0.175. Using the data from all 8 trains, there are 104 separate determinations of the proportion of water vapor in the gas stream. These are used in an ANOVA approach to obtain the following estimates. The within-laboratory standard deviation is estimated to be 0.009 with 70 degrees of freedom. The laboratory bias standard deviation estimate is 0.008 with 7 degrees of freedom. This gives a between-laboratory standard deviation estimate of 0.012.

Particulate Concentration Corrected to 12% CO_2 In order to show compliance with Federal regulations concerning incinerators, particulate concentrations are to be converted to a common base of 12 percent CO_2 by multiplying the concentration obtained by the factor 12/% CO_2, where the percent CO_2 is obtained from the stack gas analysis. The concentrations determined in the collaborative test were corrected to 12% CO_2 using the Orsat data and reanalyzed. The corrected particulate concentrations ranged from 377.1 to 1513.7 mg/scm. From the differences between the paired-train laboratories' concentrations, a within-laboratory standard deviation of 55.43 mg/scm is calculated. This represents an 8.2% variation relative to the mean level. This does not include any added effect due to determination of percent CO_2 in the gas stream, however, since these laboratories made a single stack gas analysis for both trains. A separate error term gives an estimated within-laboratory standard deviation of 96.52 mg/scm, or 14.3% of the mean, with variability due to CO_2 determination included. There are 13 and 69 degrees of freedom, respectively, for the two estimates. The laboratory bias standard deviation is estimated from differences between the independent laboratories operating on a single-paired train. The estimated value is 114.96 mg/scm with 3 degrees of freedom, or 17.0% of the mean value. The between-laboratory standard deviation is estimated separately using each of the within-laboratory estimates above. From the paired-train laboratory estimate, the between-laboratory standard deviation is 127.62 mg/scm, or an 18.8% variation. Using the ordinary ANOVA error term, the between-laboratory standard deviation is 150.10 mg/scm, giving an estimated coefficient of variation of 22.2%.

The apparent conclusion from the above is that qualified teams using the revised Method 5 and carefully following the procedural details, specified to a much greater degree than in the published method, can obtain particulate concentration measurements with reasonable precision. The precision for the associated methods appears adequate for the purposes for which they were intended, with the possible exception of the CO_2 determination. It can be seen from the corrected particulate loadings that significant variation was induced in the loadings due to variation in the CO_2 data.

Comparison is made in this report between the results of this study and those of previous studies dealing with the above variables.

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I. INTRODUCTION

This report describes the work performed and results obtained on Southwest Research Institute Project 01-3462-014, Contract No. 68-02-0626, which includes collaborative testing of the most recent revisions of Method 5 and related methods for particulate emissions in accordance with the test methods and procedures specified for municipal incinerators given in "Standards of Performance for New Stationary Sources."[2]

This report describes the collaborative testing of the most recent revisions of Method 5 and associated methods in a municipal incinerator using paired particulate sampling trains. The statistical analysis of the data from the collaborative test and the conclusions and recommendations based upon this analysis of data are presented.

II. COLLABORATIVE TESTING OF METHOD 5 AND ASSOCIATED METHODS

A. Collaborative Test Site

Arrangements were made for collaborative testing of Method 5 and associated methods at the Northeast Municipal Incinerator of the Metro Dade County Public Works Department, Miami, Florida. Arrangements for use of this site were made by Dr. William Mitchell, EPA.

The incinerator consists of a single furnace train with a capacity of 272 metric tons of refuse per 24-hour day. The furnace is a dual-grate design and is fed refuse by a hydraulic ram on an automatic time cycle. Refuse is transferred from the storage bins to the ram-charging hopper by a traveling bridge crane.

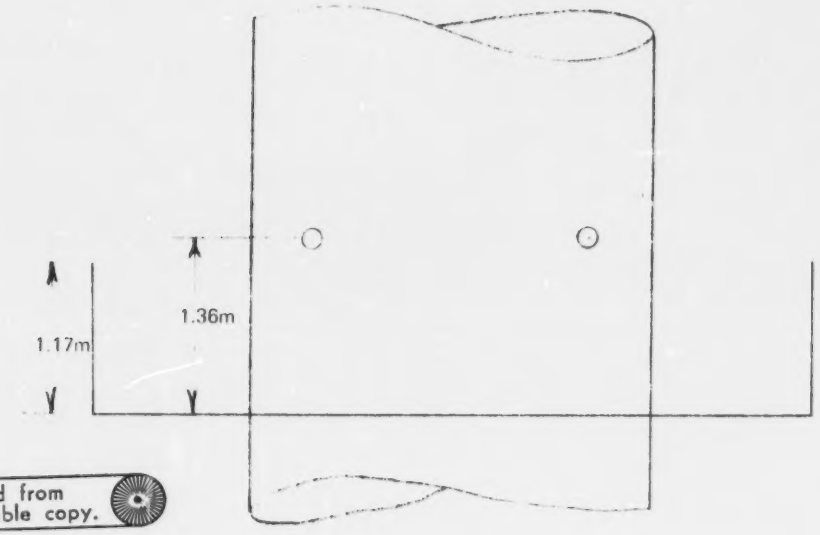
The unit is operated to maintain a furnace outlet temperature of 980°C. Gases leaving the furnace are cooled by water injection through an array of spray heads and by addition of dilution air. Water feed rates and dilution air volume are controlled by regulators which use furnace outlet temperature as a control signal. The gases are cooled to about 260°C and are then fed to an electrostatic precipitator for particulate removal. The outlet gas from the precipitator passes through an induced draft fan and is fed into the base of a 3-meter diameter stack. Due to the gas conditioning prior to the precipitator, the stack conditions were relatively uniform; stack gas velocity was about 15 meters/second, stack gas temperature was approximately 250°C, stack gas moisture content ranged around 15 percent and CO_2 concentration in the stack gas was 2.0 2.5 percent.

Four sampling ports were available. The sample ports were at 90 degrees to each other and were located 23 meters above grade. Access to the sample ports was from a square platform around the stack which was 21.6 meters above grade. The sample ports were located 19.5 meters (6.5 diameters) downstream of the stack inlet and greater than 6 meters (2 diameters) upstream of the stack outlet. This required the use of 24 traverse points, 12 on each diameter. The sample site configuration is shown in Figure 1. Figure 2 is a view of the sampling platform taken from the ground, with the 4 paired trains in place at the corners of the platform. Figure 3 shows a crew (technicians from two independent laboratories) operating a train during a sampling run. Average velocity profiles are shown in Figure 4, and a view of the unit is shown in Figure 5.

B. Collaborators

The collaborators for the Northeast Incinerator test were:

Name	Organization
Mr. Mike Taylor Mr. Nollie Swynnerton Mr. Hector Ramos	Southwest Research Institute San Antonio, Texas
Mr. Emil Stewart Mr. David Huckabee Mr. Roy Doster	Entropy Environmentalists, Inc. Research Triangle Park, N. C.
Mr. Bill DeWees Mr. John Atkins	Pedco-Environmental, Cincinnati, Ohio
Mr. Kim Thompson Mr. Pete Watson	Commonwealth Laboratory Richmond, Virginia



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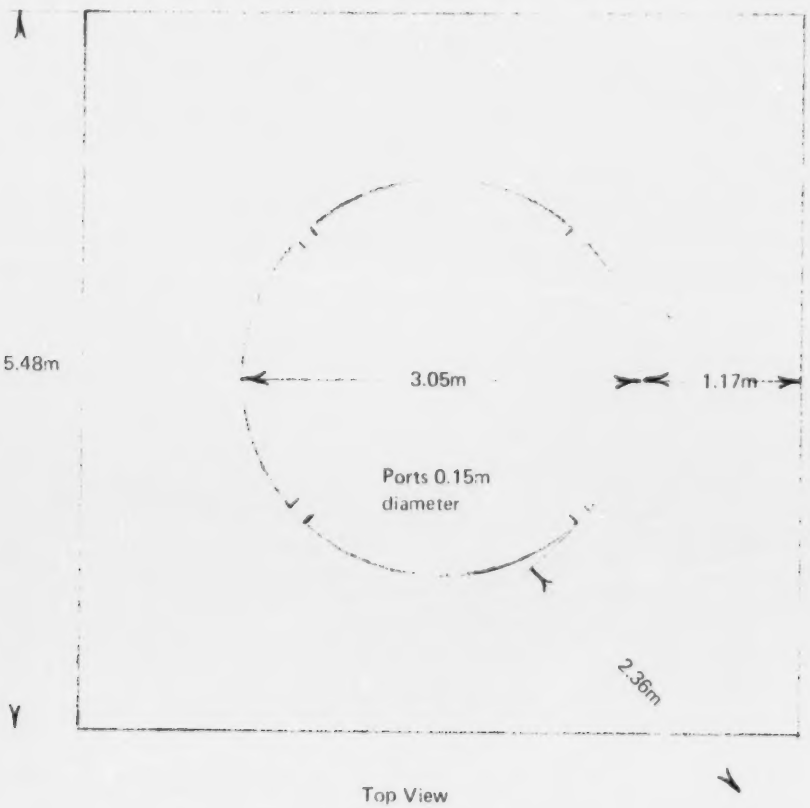
Side View



Top View

FIGURE 1. SAMPLING SITE CONFIGURATION

FIGURE 2. SAMPLING PLATFORM CONFIGURATION

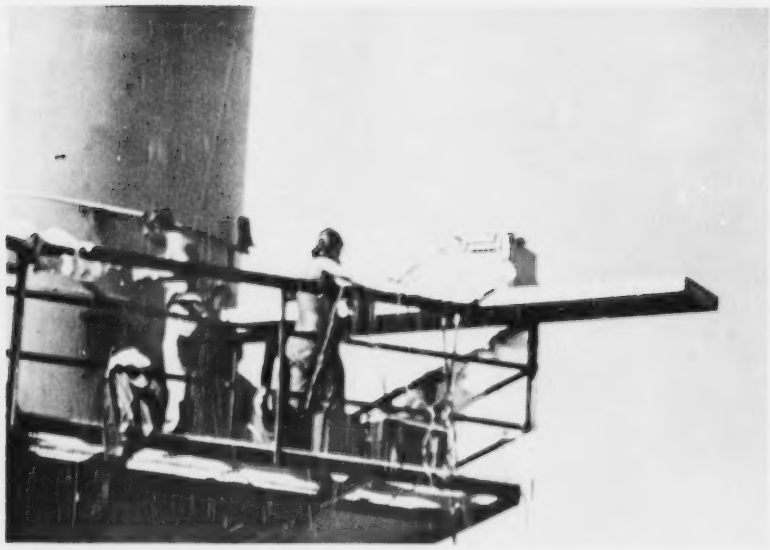
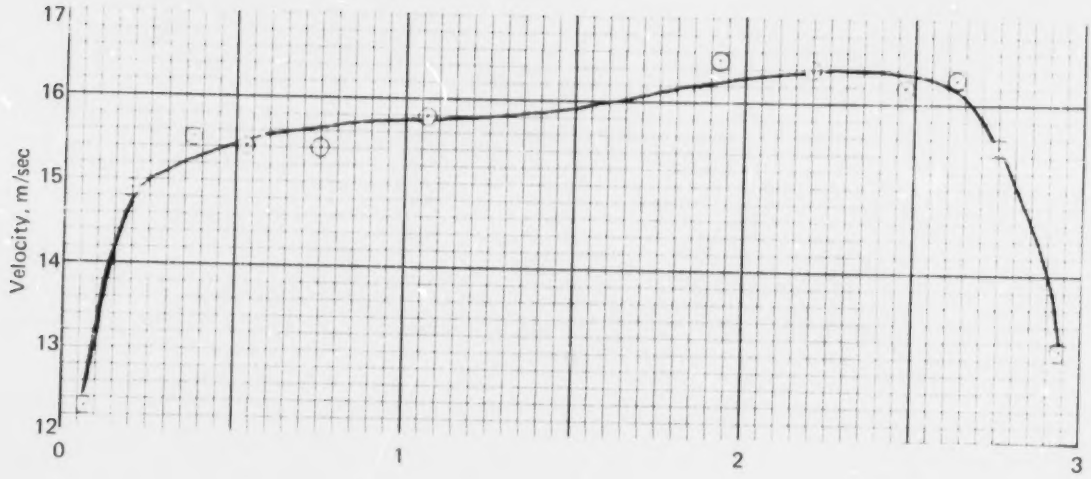
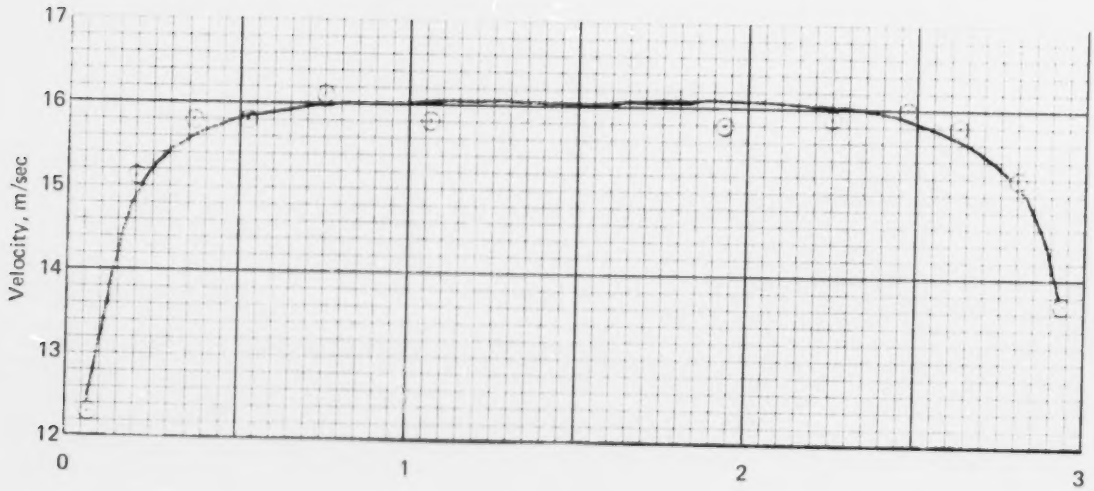


FIGURE 3. SAMPLING TRAIN OPERATION



Stack Diameter, Meters
Profile Across Ports 1–3



Stack Diameter, Meters
Profile Across Ports 2–4

FIGURE 4. AVERAGE VELOCITY PROFILES

FIGURE 5. METRO DADE COUNTY NORTHEAST INCINERATOR

Name	Organization
Mr. Barry Jackson Mr. Jeff O'Neil	Roy F. Weston, Inc. Westchester, Penn.
Mr. Al Linero Mr. Gary McRae Mr. Bill Wells	Environmental Science and Engineering, Inc. Gainesville, Florida
Mr. Joe Wilson Mr. Walt Nunes Mr. Dave Ochadlik	Scott Environmental Technology, Inc. Plumsteadville, Penn.
Mr. John Dollar Mr. Wayne Daughtry Mr. Jim Menchey	Harmon Engineering Auburn, Alabama
Mr. Bob Norton Mr. Joe Boyd Mr. Bob Missen	Pacific Environmental Services, Inc. Santa Monica, California

Note: Throughout the remainder of this report, the collaborating laboratories are referenced by randomly assigned code numbers as Lab 101 through Lab 109. These code numbers do not necessarily correspond to the above ordered listing of collaborators.

The collaborative test was conducted under the general supervision of Dr. Henry F. Hamil of Southwest Research Institute. Dr. Hamil had the overall responsibility for assuring that the test was conducted in accordance with the collaborative test plan and that the collaborators adhered to the most recent revision of Method 5.

Dr. William Mitchell, Quality Assurance Branch, EMSL, EPA, was present during the first week of the test. Mr. Rodney Midgett, Project Officer, Quality Assurance Branch, EPA, and Mr. Ed McCarley, Emission Measurement Branch, OAQPS, EPA, were present during the second week of the test.

Southwest Research Institute was provided by EPA with a list of sixteen laboratories who were current or past EPA contractors. These laboratories were considered to have the requisite experience and expertise to participate in a Method 5 collaborative test. Requests for quotation along with a scope of work statement were submitted to all sixteen laboratories. Fourteen responses were received, and the eight low bidders were accepted for the collaborative test.

C. Pretest Calibration Requirements

Improper calibration of test equipment or changes in calibration factors after laboratory calibration and prior to the test can be sources of imprecision in Method 5 determinations. In order to minimize any effect on the test results due to equipment calibration, the collaborators were required to provide Southwest Research Institute with their calibration data prior to the start of the test. Meter box calibrations and pitot tube calibrations were carried out as specified in the revised methods and in accordance with the procedures specified by Rom.[10] Calibration data for meter boxes and pitot tubes were reported on the forms shown in Figure 6 and Figure 7, respectively.

Prior experience had shown that commercially available nomographs were not always reliable, due to misalignment of the various scales on the nomographs. Calibration checks of the nomographs used by the collaborators were required, using the procedure of Shigehara.[13] The nomograph calibration reporting form is shown in Figure 8. Each collaborator was required to have a spare nomograph to avoid any delays in the test due to damage to a nomograph.

As a further check on meter box calibrations, and to determine if any calibration changes had occurred during shipment, a two-point calibration check of all meter boxes was conducted at the test site prior to the start of the test. Southwest Research Institute provided a calibrated dry gas meter to be used as a standard during this calibration check. This dry gas meter was calibrated against a spirometer just prior to the test.

The two calibration check points were selected to span the range of Δp expected during the test. Three meter boxes were found to be outside the allowable specifications for dry gas meter calibration according to the revised method ($\gamma = 1.00 \pm 0.02$). One meter box was corrected by replacement of the dry gas meter with a spare meter. The other two meter boxes were recalibrated in the field, using the Southwest Research Institute "standard" dry gas meter. After this recalibration, one meter box was found to have an orifice coefficient (ΔH) outside the allowable range. The orifice was replaced with a spare which met the calibration specifications.

Calibration requirements for the pitot tubes specified that the calibration be performed with the complete pitobe assembly using a 3/8-inch nozzle. All laboratories except one had pitot coefficients in the acceptable range (0.85 ± 0.02). The one laboratory whose pitot tube coefficient was outside the allowable range used the adjustment equation described by Shigehara[13] to obtain a proper nomograph C factor for their pitot tube coefficient.

All collaborators had the required number of acceptable nomographs, checked by the procedure of Shigehara[13].

D. Conduct of the Test

The purpose of this collaborative test was to estimate the minimum variability that can be expected from Method 5 (revised) when used in accordance with the applicable test methods and procedures specified for the source tested. Additionally, the test was structured to allow determination of any noticeable effect in the results of a field test due to spatial/temporal changes in particulate concentration due to changing stack gas flow patterns.

Previous collaborative tests of Method 5 [3,4,5] involved four collaborating laboratories using conventional Method 5 trains. Each team sampled all ports sequentially, using either radius or diameter

Calibration Check: Orifice Meter and Dry Gas Meter

Laboratory _____ Meter Box _____

Date _____ Primary Standard _____

Barometric Pressure, P_b = _____ in Hg

Orifice Manometer Setting, ΔH in H_2O	Gas Volume Primary Standard V_w (ft^3)	Gas Volume Dry Gas Meter V_d (ft^3)	Temperatures				Time θ (min)	γ	$\Delta H@$
			Primary Standard, t_w (°F)	Dry Gas Meter					
				Inlet t_{d_i} (°F)	Outlet t_{d_o} (°F)	Average t_d (°F)			
0.2									
0.3									
0.4									
0.5									
0.6									
0.7									
0.8									
0.9									
1.0									
2.0									
3.0									
4.0									
							Average		

Calculations

ΔH	γ	$\Delta H@$
	$\dfrac{V_w P_b (t_d + 460)}{V_d \left(P_b + \dfrac{\Delta H}{13.6}\right)(t_w + 460)}$	$\dfrac{0.0317\ \Delta H}{P_b (t_d + 460)} \left[\dfrac{(t_w + 460)\theta}{V_w}\right]^2$
0.2		
0.3		
0.4		
0.5		
0.6		
0.7		
0.8		
0.9		
1.0		
2.0		
3.0		
4.0		

FIGURE 6. METER BOX CALIBRATION FORM

Calibration Check: S Type Pitot Tube

Reference: Revised Method 2 Draft

Laboratory _____

Pitot Tube Identification Number: _____

Date: _____

Calibrated by: _____

"A" Side Calibration

Run No.	Δp_{std} cm H_2O (in. H_2O)	$\Delta p_{(s)}$ cm H_2O (in. H_2O)	$C_{p(S)}$	Dev.
1				
2				
3				
		Average		

"B" Side Calibration

Run No.	Δp_{std} cm H_2O (in. H_2O)	$\Delta p_{(s)}$ cm H_2O (in. H_2O)	$C_{p(S)}$	Dev.
1				
2				
3				
		Average		

Dev. = $C_{p(S)}$ $C_{p(S)(avg.)}$ = _____ (Must be ≤ 0.01)

C_p Difference: A_{avg} - B_{avg} = _____ (Must be ≤ 0.01)

FIGURE 7. PITOT TUBE CALIBRATION FORM

Calibration Check: Nomograph

Laboratory _____

Date _____

(1) *C* Factor Adjustment

Probe 1	Probe 2	Probe 3
C_p = _____	C_p = _____	C_p = _____

If $C_p > 0.87$ or $C_p < 0.83$

Probe 1	Probe 2	Probe 3
$C_{adj} = C\frac{C_p^2}{(0.85)^2}$	$C_{adj} = C\frac{C_p^2}{(0.85)^2}$	$C_{adj} = C\frac{C_p^2}{(0.85)^2}$
$= C\frac{(\quad)^2}{(0.85)^2}$	$= C\frac{(\quad)^2}{(0.85)^2}$	$= C\frac{(\quad)^2}{(0.85)^2}$
$= C(\quad)$.	$= C(\quad)$.	$= C(\quad)$.

(2) Accuracy

(a) *K*-factor line, ΔH and Δp scales

Aline	Set	ΔH Reading: Nomograph 1	ΔH Reading: Nomograph 2
$\Delta p = 0.001$; $\Delta H = 0.1$	$\Delta p = 0.01$ $\Delta p = 0.1$		
$\Delta p = 10.0$; $\Delta H = 10.0$	$\Delta p = 1.0$ $\Delta p = 0.1$		
$\Delta p = 0.1$; $\Delta H = 1.0$	$\Delta p = 1.0$ $\Delta p = 0.01$		

(b) *C*, t_s and D_n scales

C	D_n	t_s (°F)	Δp	ΔH Readings: Nomograph 1	ΔH Readings: Nomograph 2
2.0	0.5	2500	0.02		
1.5	0.4	1500	0.8		
1.0	0.3	1000	0.1		
0.7	0.25	500	3.0		
0.5	0.2	200	0.9		

FIGURE 8. NOMOGRAPH CALIBRATION FORM

traverses as required by the sampling site configuration. Each team sampled all the sample points, but at different times. Therefore, any variation in results due to spatial/temporal changes in the particulate concentration would be incorporated into the precision estimates for the method. Also, since the true particulate concentration in these tests was not known, it could not be assumed that day-to-day samples obtained by the laboratories were replicates. It was necessary to block the test data before statistical analysis, using plant operating data as the blocking criterion. However, the plant operating data were only indicators of changing particulate concentrations and gave no true measure of the concentration itself.

The present test involved a total of nine collaborating laboratories using paired particulate sampling trains. The paired particulate sampling trains consist of two mirror-image Method 5 sample boxes on a common base. Each half of the train consists of a probe support, heated filter oven, impinger train, icebath and sample head. Aside from the base, there is no commonality in the trains. The pitobe assemblies are mounted to give a separation of 5.8 cm between the sample nozzles. Probes are mounted so that the pitot tubes are outboard relative to each other. Figure 9 shows a paired particulate sampling train in position for a sampling run with probes in place and umbilicals connected. The dimensions and glassware layout of the dual sample box are presented in Figure 10, while overall views are presented in Figure 11.

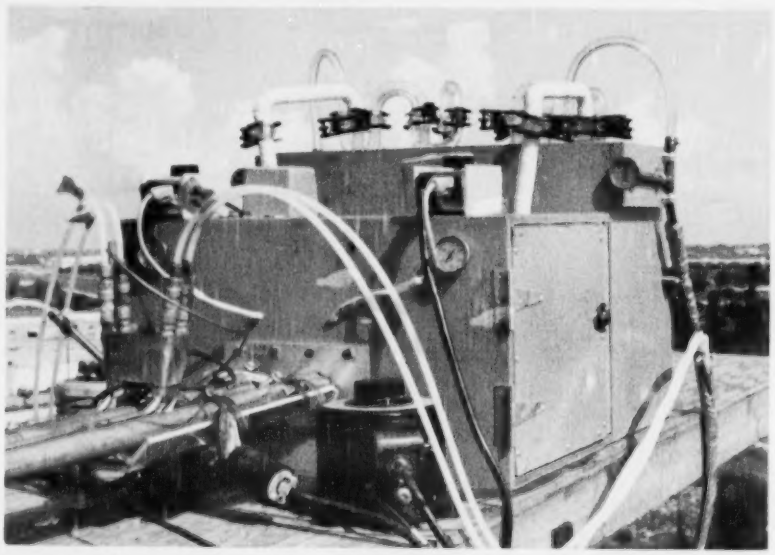
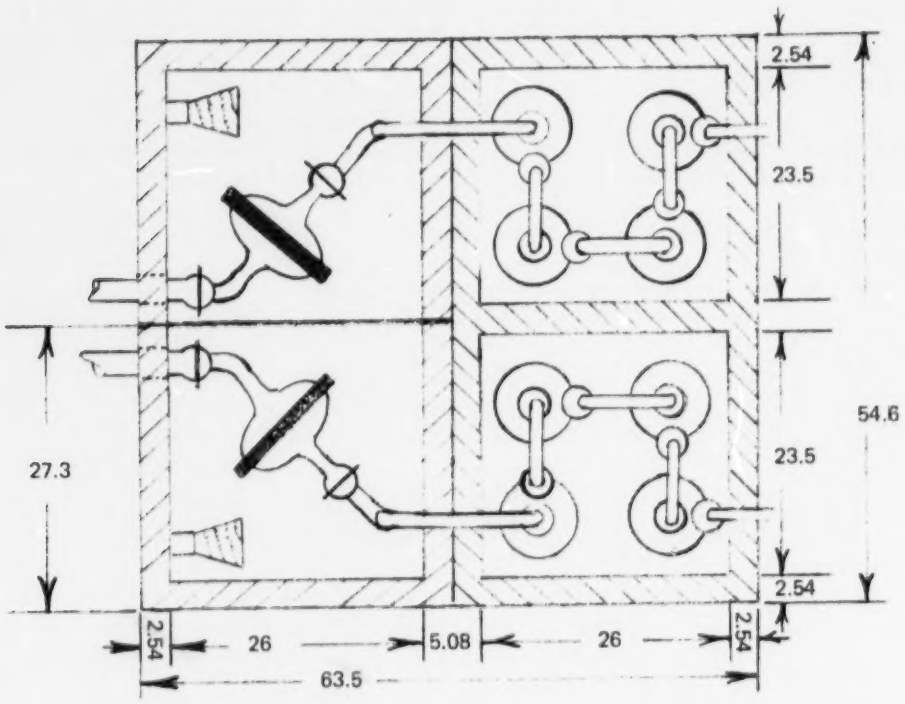


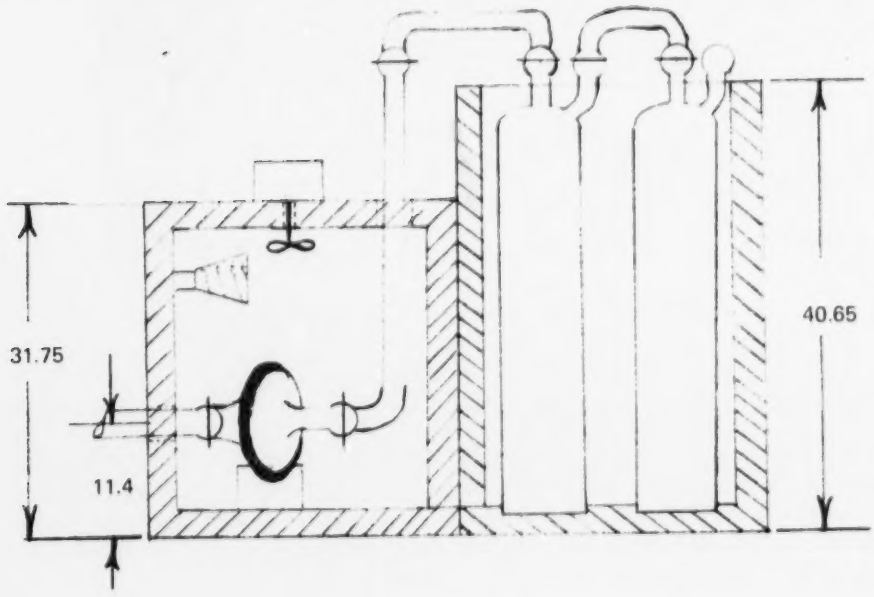
FIGURE 9. PAIRED PARTICULATE SAMPLING TRAIN

The individual filter ovens are fitted with circulating fans. Oven heat is provided by electrical resistance heaters with solid-state variable power supplies. Oven temperatures are manually controlled. Oven temperature and impinger outlet temperature are obtained using bimetallic dial-indicating thermometers. Probe heat is controlled using variable transformers. Probe temperature versus transformer settings were calibrated by each laboratory according to Rom.[10] Stack gas temperature is determined by thermocouple readout. Umbilicals containing a vacuum line, pitot lines, and an Orsat sample line were fabricated. All electrical connections to the dual sample boxes are separate from the umbilical.

Southwest Research Institute provided the paired particulate sampling trains along with special glassware (filter holders and filter holder-to-impinger train connectors) and umbilicals. Collaborating laboratories provided their own probes, pitot tubes, meter boxes, impinger trains, filters, silica gel and other normal sampling supplies and equipment. All laboratories except one provided their own gas sampling equipment to obtain integrated gas samples for Orsat analysis.



Top View



Side View

Note: Dimensions in centimeters.

FIGURE 10. DUAL SAMPLE BOX - DIMENSIONS AND GLASSWARE LAYOUT

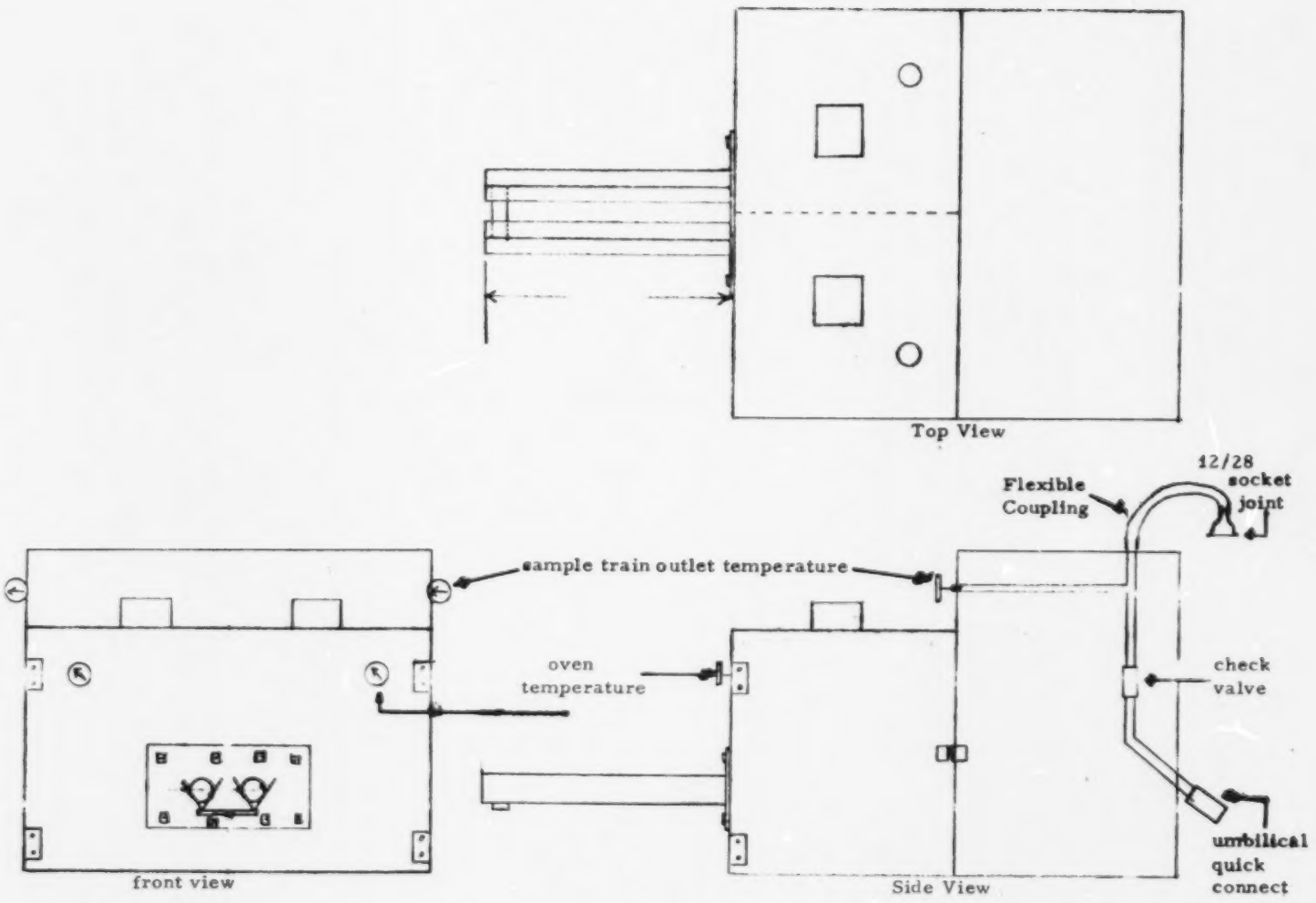


FIGURE 11. DUAL SAMPLE BOX

The test plan called for a 1-day orientation session and equipment calibration check, and a 3-week test. A total of 15 sampling runs were planned, five runs per week. Sampling was restricted to Monday through Friday since the incinerator did not operate on weekends. Four paired particulate sampling trains were used, with seven laboratories each week. One laboratory operated one paired train, with a single operator running both meter boxes. Three independent laboratories, one per week of sampling, were used on this train. The remaining six laboratories were randomly paired, and each of these laboratories operated one side of a paired particulate sampling train. The pairings of these six laboratories were unchanged for the entire three weeks of the test. This sampling scheme provided for eight separate determinations of particulate concentration on each run.

This test plan, utilizing paired particulate sampling trains, circumvents some of the drawbacks encountered in previous Method 5 tests. Four pairs of samples are obtained on each run, one sample pair taken by a single laboratory, and three sample pairs taken by three pairs of laboratories. Each of these pairs of samples should be free of any effect of spatial/temporal variation on particulate concentration during the run.[8,9] Therefore, the paired-laboratory samples allow an estimation of laboratory effect which is not influenced by any particulate variation during the run, while the single-laboratory sample pair allows estimation of sampling error by using this sample pair as a replicate measurement. Additionally, the use of paired trains allows concurrent sampling by up to eight laboratories. Previous collaborative tests were restricted to use of only four laboratories sampling concurrently due to the configuration of the sampling site and the use of standard Method 5 sampling trains. A detailed discussion of the statistical model and analytical design for this test is contained in Appendix B.1.

As stated above, the test plan called for fifteen sampling runs, five per week for three weeks. Thirteen runs were made, three the first week, and five each the second and third weeks. One run was lost due to severe weather conditions, and the other was lost due to a malfunction in the electrostatic precipitator which forced a unit shutdown.

Some problems with equipment were encountered. One laboratory used a meter box equipped with Magnahelix™ differential pressure gauges. On the initial velocity traverse, it was observed that a high Δp (0.55 in H_2O) was obtained on the velocity head gauge compared to Δp valves of around 0.40 inch H_2O for the other laboratories. Substitution of an inclined manometer for the Magnahelix™ gauge gave Δp readings comparable to those obtained by the other laboratories. Another laboratory obtained low Δp readings (0.3 in. H_2O). The pitot lines were checked for obstructions or leaks but none were found. Further investigation led to discovery of a leak in the low-pressure line between the pitot line quick-connects and the inclined manometer in the meter box. Other problems arose due to lack of familiarity of some laboratories with the revised version of Method 5 being tested. Incorrect assembly of the pitobe was noted in several cases; errors in the relative positions of the sample nozzle, pitot tube, Orsat sample tube and stack temperature thermocouple specified in the revised method to avoid sample nozzle and pitot tube interferences were observed and corrected. Use of improper equipment and techniques (plastic wash bottles, plastic probe wash containers, failure to properly cap both ends of the probe prior to moving the probe from the sample site to the clean up area) were observed and called to the attention of the collaborators for correction.

Two operational problems were encountered. The new leak check requirements in the revised method led to a number of delays in sampling runs. The collaborators chose to leak check through the sample probes to avoid removing the probe after each traverse. Numerous leaks were discovered. Most of these leaks developed in the front packing gland where the probe liner to sample nozzle seal is effected. Several types of packing were used by the collaborators, with Teflon ferrules being the most satisfactory. However, several probe liners were broken in the initial pre-run leak check due to collaborators overtightening the packing gland in attempts to stop small leaks. No probe liners were broken during the course of a run. However, one probe liner was apparently broken after completion of the sampling run and prior to sample recovery. A second problem was encountered with the leak check procedure required in the integrated gas sampling procedure in revised Method 3, which calls for checking the system at 250 mm Hg vacuum. A

variety of diaphragm pumps were used by the collaborators, and the vacuum which could be pulled varied from about 100 mm to about 350 mm Hg. As a result, some leak checks were conducted at less than 250 mm Hg.

During the test, three laboratories found it necessary to change personnel in their sampling crews. These changes were made in two cases by having the replacement arrive at the site one day before the departing person left so that a one-day orientation was available before the replacement started work on his own. In the estimation of the test supervisor, the performance of the crews with replacement was as good as with the original crews, and in one case, a significant improvement in team performance was observed.

E. Philosophy of Collaborative Testing

The concept of collaborative testing followed in the previous tests[3-7] involved conducting the test in such a manner as to simulate "real world" testing as closely as possible. "Real world" testing implies that the results obtained during the test by each collaborator would be the same results obtainable if he were sampling alone, without outside supervision, and without any additional information from outside sources, i.e., test supervisor or other collaborators.

The function of the test supervisor in such a testing scheme is primarily to see that the method is adhered to as written and that no individual innovations are incorporated into the method by any collaborator. During the test program, the test supervisor observed the collaborators during sampling and sample recovery. Any deviations from the method as written were pointed out to the collaborator by the test supervisor for correction. However, if random experimental errors in sampling and sample recovery were observed, no interference was made by the test supervisor.

The present test was designed to estimate the minimum error in the revised method. As a result, the test supervisor played a more active role, in order to minimize random errors in sampling and sample recovery, and to assure that the collaborators met the constraints of revised Method 5 and the associated Methods 2 and 3.

The increased level of supervision, the increased emphasis on collaborator qualifications, more stringent quality control of pretest equipment calibration and field checks of selected calibration factors were all implemented to allow estimation of the minimum variability of the revised Method 5.

F. Acknowledgements

Southwest Research Institute wishes to acknowledge the assistance of Dr. William Mitchell, Quality Assurance Branch, EPA, who made the arrangements for the use of the test site. Dr. Mitchell also provided assistance to the test supervisor during the first week of the test.

Appreciation is given to the Metro Dade County Public Works Department, Miami, Florida, for use of their Northeast Municipal Incinerator as a test site. This appreciation is extended especially to Mr. Bud Hill and his staff at the incinerator for their assistance and cooperation both during site preparation and the conduct of the test.

III. STATISTICAL ANALYSIS

A. Definitions and Terms

To facilitate the understanding of this report and the utilization of its findings, this section explains the statistical terms used in the report. The estimates of the pertinent values and the details of the methods used to obtain them are contained in subsequent sections.

We say that an estimator, $\hat{\theta}$, is *unbiased* for a parameter, θ, if the expected value of $\hat{\theta}$ is θ, or in notational form, $E(\hat{\theta}) = \theta$. Let $X_1, X_2, \ldots, X_n$ be a sample of size n from a population of method determinations. Then we define:

(1) $\bar{X} = \frac{1}{n}\sum_{i=1}^{n} X_i$ –the sample mean, an unbiased estimate of the true mean determination. The sample mean estimates the center of the distribution of X.

(2) $s^2 = \frac{1}{n-1}\sum_{i=1}^{n} (X_i - \bar{X})^2$ –the sample variance, an unbiased estimate of the population variance, σ^2. The sample variance estimates the dispersion in the distribution of X.

(3) $s = \sqrt{s^2}$ –the sample standard deviation, a biased[14] estimate of σ, the population standard deviation. The sample standard deviation is an alternative estimate of dispersion. To remove the bias in s, a factor of α_n, dependent on the sample size, is used, so that $E(\alpha_n s) = \sigma$.

(4) $\beta = \frac{\sigma}{\mu}$ –the true coefficient of variation. The sample coefficient of variation, $\hat{\beta}$, is estimated by the ratio of the two unbiased estimates, $\hat{\beta} = \frac{\alpha_n s}{\bar{X}}$.

The precision components are estimated for this report by one of two methods. For the majority of the data, an Analysis of Variance (ANOVA) procedure is used. This is a test for the equality of means of several groups utilizing the estimated variance components for the various factors in a model. The ANOVA is generally summed up in a table which contains the following information.

(5) **df**–degrees of freedom, an indication of the degree of confidence in the estimate. The more df, the higher the degree of confidence one has in an estimated variance component.

(6) **SS**–sum of squares. The SS represents the squared deviations from the mean of a particular group.

(7) **MS** = SS/df-mean square. The MS is a variance estimate, similar to the s^2 estimate above. The MS of a factor is used both to estimate its variance component and to test for significance.

(8) **F**–F-ratio. The ratio of a mean square to its appropriate denominator. A large F-ratio implies a difference among means for a term in the ANOVA, and the existence of a variance component for that factor.

(9) **EMS**–expected mean square. The expected value of MS, which allows the proper F-ratio to be formed and variance components to be estimated.

The second technique is referred to as a coefficient of variation approach. In this, the model used is one in which the standard deviation is assumed to be proportional to the mean value. The coefficients of variation, then, are estimated for the components of interest and standard deviations expressed as a constant times an unknown mean. The estimates take the form of (4) above and are weighted, if necessary, and averaged into a single value.

The precision components for this report will be expressed in terms of standard deviations. The principal components will be:

σ_b – between-laboratory standard deviation. This represents the total variation in a result, composed of within-laboratory and laboratory bias components. The between-laboratory variance can be written as

$$\sigma_b^2 = \sigma^2 + \sigma_L^2$$

σ–within-laboratory standard deviation. This represents the ordinary sampling error in replicates made at the same true level by the same laboratory team.

σ_L –laboratory bias standard deviation. This represents the variation that can be expected between two independent laboratory teams determining results at the same true level, μ. This variation is attributable to such factors as different operators, equipment and analysts.

B. Particulate Test Data

For the statistical analysis, the paired-train laboratories are designated Labs 101, 102 and 103. Labs 104 and 105 operated on the same paired train as did Labs 106 and 107 and Labs 108 and 109. There were 13 sampling runs made in all, and 104 determined particulate concentrations. These were spot-checked for their calculation accuracy and adjusted where necessary. The only values that required recalculation were those from laboratories that use a standard computer program to obtain the results of the test. Since the revised method specifies that standard temperature be 20°C (68°F), the constants for calculating both standard metered volume and standard water volume changed slightly. In these cases, the volumes and particulate loadings required recalculation. The checked and recalculated data are shown in Table 1.

TABLE 1. PARTICULATE CONCENTRATION, mg/scm

Run	Labs											
	101		102		103		104	105	106	107	108	109
	A	B	A	B	A	B						
1	117.9	132.6					189.5	122.3	139.0	137.8	135.2	126.2
2	100.8	106.1					129.9	79.4	100.1	87.8	123.0	103.6
3	128.5	135.7					143.9	135.0	124.4	116.7	101.3	107.1
4			144.1	148.1			155.8	151.0	142.6	135.6	141.6	123.5
5			103.4	112.3			120.3	124.7	110.7	107.2	119.1	123.6
6			150.9	133.3			149.3	123.3	145.7	142.1	176.6	159.9
7			81.9	81.7			101.2	129.4	91.2	86.2	99.3	82.2
8			101.3	104.2			137.2	114.1	119.9	116.9	140.2	95.9
9					101.2	107.6	97.4	108.1	97.6	89.2	94.7	90.2
10					157.3*	158.1	158.1	144.2	146.4	140.1	136.2	171.8
11					169.9	161.3	162.8	124.4	157.6	155.1	177.4	152.8
12					254.5	190.2	164.1	146.7	152.0	148.1	154.7	137.8
13					188.6	189.9	185.1	157.4	159.5	154.7	163.8	139.1

*Substituted value.

There is one value in the table that is not an actual method determination, that made by Lab 103 in Run 10. The actual reported value was 205.5 mg/scm, but it was noted that the collaborator had detected a broken probe at the end of the run, and that the material collected on the filter was of an unusual nature. As a result, the value was eliminated, and the data point replaced using the technique of Yates, as given in Snedecor and Cochran[14]. While not the most desired option, it is necessitated by the choice of model for the ANOVA.

In previous collaborative tests of Method 5, there has been a tendency toward occasional high values which have adversely affected the precision estimates obtained. It was noted[2] that there was generally a tendency for the acetone wash to contain an unusually high percentage of the total particulate collected. As a check on the data from this test, the percentages of total particulate collected from the acetone wash were calculated, and these are shown in Table 2.

TABLE 2. PERCENTAGE OF COLLECTED MASS IN ACETONE WASH

Run	Labs											
	101		102		103		104	105	106	107	108	109
	A	B	A	B	A	B						
1	31.0	33.5					44.3	51.0	28.3	31.2	52.1	45.7
2	21.9	34.7					50.1	59.3	42.8	30.6	50.6	32.6
3	20.9	30.5					49.2	48.8	19.9	25.5	38.6	35.5
4			22.1	12.6			53.2	49.0	27.6	32.1	42.9	40.2
5			29.4	21.9			50.8	47.5	13.8	24.4	45.2	51.7
6			34.1	19.1			50.9	53.5	19.7	33.6	50.3	64.6
7			19.7	22.8			51.6	68.5	24.0	29.7	43.8	47.8
8			19.0	17.8			50.6	51.4	27.6	31.9	34.8	32.6
9					40.1	29.0	48.5	48.4	21.5	25.8	40.2	48.2
10					45.0*	43.1	52.1	52.9	30.0	28.1	46.7	52.4
11					51.5	38.8	47.7	65.4	21.9	27.9	45.7	40.0
12					72.7	46.0	56.1	59.5	38.2	27.2	39.5	33.7
13					58.1	44.8	57.3	52.9	31.1	30.0	36.7	35.5

*Concentration not used in subsequent analyses.

As can be seen, the percentages are fairly consistent within any single laboratory's data. The amount of particulate in the acetone wash is related to the length of the probe. Since the pairs of laboratories used probes of approximately equal length, the laboratories working on the same paired train show similar percentages.

The data are analyzed using a two-way ANOVA, with the run and laboratory terms as factors, and the interaction between the two taken to be zero. The model is discussed in detail in Appendix B.1. The data are treated first according to the three separate weeks using 7 laboratories and 8 trains, then for the entire 13 sampling runs using only the six laboratories who participated in the entire test. Where appropriate, contrasts among the means of the laboratories are used to determine the sources that contributed to the variation in a Method 5 concentration determination. The precision of a method result and the conclusions that can be drawn from the data are discussed below. In addition, the data are treated as if they were results for a compliance test, and corrected to 12% CO_2, as called for in the test methods and procedures section of the *Federal Register* pertaining to incinerators.[2] These values are submitted to analysis according to the same model as the uncorrected particulate concentrations, and the results discussed in a subsequent section.

C. Precision of Method 5

The particulate concentration determinations are used to estimate standard deviations for within-laboratory and laboratory bias components, and from these, the between-laboratory term is estimated. The three ANOVA's, one per week of the test, are used to obtain the estimated within-laboratory term.

TABLE 3. ESTIMATED PRECISION BETWEEN PAIRED-TRAIN LABORATORIES

Lab	SS	df	MS	$\hat{\sigma}$	$\hat{\beta}$, %
101	148.01	3	49.34	7.03	5.8
102	206.71	5	41.34	6.43	5.2
103	2125.87	5	425.17	20.62	13.9
Pooled	2480.59	13	190.81	13.81	10.4

There are two possible estimates of the within-laboratory variance. One is obtained from the two trains being operated by a single laboratory. A sum of squares is calculated between the two trains for each run, with 1 df per run as a result. The estimated variances are shown in Table 3 for the three dual train laboratories. Testing for the equality of variance among the three estimates shows that they can be considered equal at a significance level of 0.03. This would allow the pooled estimate to be used.

Similarly, the run by lab interaction term is an estimate of sampling error under the assumptions of the model. There are three estimates of σ^2 using the interaction mean square and these are shown in Table 4.

TABLE 4. ESTIMATED WITHIN-LABORATORY COMPONENTS FROM INTERACTION TERM

Week	SS	df	MS	$\hat{\sigma}$	$\hat{\beta}$, %
1	2,867.98	14	204.86	14.31	11.7
2	4,419.77	28	157.85	12.86	10.4
3	9,236.25	27	342.08	18.50	12.4
Composite	16,524.00	69	239.48	15.48	11.7

Using Bartlett's test, the three mean squares are tested to see if they are estimating the same true variance. The significance level of the test is 0.13, so the hypothesis of equality is accepted. This allows the use of the pooled estimate, which has the greater df. Comparing the composite mean squares from Tables 3 and 4, it can be seen that while the second is larger, the two are close to one another and thus are probably estimating the same true variance, σ^2.

In view of the definition of the within-laboratory term, however, the estimate from between the trains operated by a single laboratory team is selected. Since both trains were sampling essentially the same gas stream at the same time, this variability most nearly conforms to the concept of a replicate. In Appendix B.2, contrasts are used to test that the two trains were getting equivalent measurements, and the hypothesis is accepted for each of the three labs.

The estimated within-laboratory variance, then is

$$\hat{\sigma}^2 = MS_{pooled}$$
$$= 190.81$$

with 13 df. The estimated within-laboratory standard deviation is

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$
$$=$$
$$= \sqrt{190.81}$$
$$= 13.81 \text{ mg/scm.}$$

and using the overall mean, $\hat{\mu}$, of 132.66, this gives an estimated coefficient of variation of

$$\hat{\beta} = \hat{\sigma}/\hat{\mu}$$
$$= 13.81/132.66$$
$$= 0.104.$$

In terms of relative variation, then, replicate measurements by a single laboratory would have a standard deviation of 10.4% of the mean value. Previous tests in which the concentrations varied over a wider range than in this one indicated that the percentage variation was a valid model for a Method 5 result.

The laboratory bias variance is estimated from the labs term in the 3-week, 6 laboratory ANOVA. The sums of squares for labs is partitioned by means of orthogonal contrasts into SS for the differences between the single-laboratory pairs. These represent variation between independent laboratories sampling the same gas stream at the same time. The three SS are

$$SS_1 = 2117.72$$

$$SS_2 = 184.66$$

and

$$SS_3 = 858.13,$$

each with 1 df. Pooling these gives an estimated mean square of

$$MS_{pooled} = \frac{SS\ pooled}{df\ pooled}$$

$$= \frac{3160.51}{3}$$

$$= 1053.50$$

Using the EMS of this term, the laboratory bias variance is estimated as

$$\hat{\sigma}_L^2 = 66.36$$

with 3 df. This gives a laboratory bias standard deviation of

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}_L^2}$$

$$= \sqrt{66.36}$$

$$= 8.15 \text{ mg/scm.}$$

In terms of relative variation, a coefficient of variation may be estimated for the laboratory bias component. This gives

$$\hat{\beta}_L = \hat{\sigma}_L / \hat{\mu}$$

$$= 8.15/132.66$$

$$= 0.061$$

or 6.1% of the mean value.

The laboratory SS is also partitioned to test whether a difference exists between pairs of laboratories. There has been speculation that differences among labs result from the fact that the labs sample the points at different times and that these differences result from a changing particulate loading during the course of a two-hour run. If this is the case, there should be a noticeable difference between the pairs of laboratories.

There was no significant difference among the pairs of trains in the three individual weeks analyses. For the 6-laboratory analysis, the pairs term was significant, but the mean square partitioned out of the labs term for pairs is indistinguishable from the mean square for between paired labs shown above. The conclusion, then, is that this difference is due to laboratory differences unrelated to the sampling location of the pairs.

The lack of a difference among pairs by itself does not assure that there was no effect due to changing particulate loading. The comparison of the mean values could mask out fluctuations in the values during the course of the runs that were related to the order of sampling the four ports. If these gas stream-related fluctuations occur, then the error term associated with the differences between pairs should be significantly different from the sampling error estimated for replicate particulate determinations. The error mean square for pairs is 257.28, with 12 df. Using an F-ratio test to compare this to the estimated within-laboratory variance, the difference is not significant. Thus there is no evidence that the differences among laboratories for this test are related to the changing pattern of particulates flowing in the gas stream, due to differences in the time a particular point is sampled. Thus, for this test site, spatial/temporal effects in the stack gas stream did not contribute to the variability in the particulate concentration determinations.

The between-laboratory variance, σ_b^2, thus is composed of only within-laboratory and laboratory bias terms. The estimate from the above terms is

$$\hat{\sigma}_b^2 = \hat{\sigma}^2 + \hat{\sigma}_L^2$$

$$= 190.81 + 66.36$$

$$= 257.17,$$

which gives a between-laboratory standard deviation of

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}_b^2}$$

$$= 16.04 \text{ mg/scm.}$$

There are 3 df associated with this estimate, due to the laboratory bias term. The estimated coefficient of variation, then, is

$$\hat{\beta}_b = \hat{\sigma}_b / \hat{\mu}$$

$$= 16.04/132.66$$

$$= 0.121 \text{ mg/scm}$$

or 12.1% of the mean value.

D. Rank Test for Equality of Laboratories

An alternative technique for determining if all laboratories were obtaining the same concentration is by applying a rank test to the data. The purpose of this test is to indicate whether there are differences among the labs where the distributional nature of the determinations is unspecified.

The test selected is the Friedman[12] test, which allows for a blocking factor, in this case runs. to be included. The data are analyzed first with 7 laboratories for each week of testing, then with 6 laboratories for the full 13 runs. The details of the analyses are described in Appendix B.3.

The ranks of the data are shown in Table 5 for the separate weeks and in Table 6 for the 6 labs through three weeks. The significance levels obtained for the three separate weeks indicate that during the first week there was no perceptible rank ordering, while the second week showed some order tendency and the third showed a marked tendency. However, looking at the six labs who participated in all 13 runs, the probability of obtaining those rank sums due to chance alone is approximately 1 in 1000.

Lab 104 showed a strong tendency toward giving higher results than the other 6 laboratories, with 6 determinations having the highest values and no determination being in the lower half of the six values on a given run. At the opposite end, Lab 107 has only one determination among the three highest observations in a run, while Lab 106 tends toward the middle of the 6 on all runs. If these differences are due to the pattern of the particulates flowing in the gas stream, then the pairs of trains should be similar. In fact, however, they are not. In contrast to Lab 104, Lab 105 has a mix of high and low values. The dissimilar results from Labs 106 and 107 are from a paired train, and the ranks between Labs 108 and 109 appear unrelated to each other.

The apparent conclusion, then, is that the differences between labs result not from the pattern of the gas flow but from lab-to-lab differences in such things as the equipment used and the procedures followed in obtaining a Method 5 result.

TABLE 5. RANKS OF CONCENTRATION DETERMINATIONS–INDIVIDUAL WEEKS

Run	Labs						
	101	104	105	106	107	108	109
1	6	1	7	2	3	4	5
2	4	1	7	5	6	2	3
3	3	1	2	4	5	7	6
Sums	13	3	16	11	14	13	14
	Labs						
	102	104	105	106	107	108	109
4	3	1	2	4	6	5	7
5	6	3	1	5	7	4	2
6	5.5	3	7	4	5.5	1	2
7	7	2	1	4	5	3	6
8	6	2	5	3	4	1	7
Sums	27.5	11	16	20	27.5	14	24
	Labs						
	103	104	105	106	107	108	109
9	2	4	1	3	7	5	6
10	2.5	2.5	5	4	6	7	1
11	2	3	7	4	5	1	6
12	1	2	6	4	5	3	7
13	1	2	5	4	6	3	7
Sums	8.5	13.5	24	19	29	19	27

TABLE 6. RANKS OF CONCENTRATION DETERMINATIONS–THREE WEEKS DATA

Run	Labs					
	104	105	106	107	108	109
1	1	6	2	3	4	5
2	1	6	4	5	2	3
3	1	2	3	4	6	5
4	1	2	3	5	4	6
5	3	1	5	6	4	2
6	3	6	4	5	1	2
7	2	1	4	5	3	6
8	2	5	3	4	1	6
9	3	1	2	6	4	5
10	2	4	3	5	6	1
11	2	6	3	4	1	5
12	1	5	3	4	2	6
13	1	4	3	5	2	6
Sum	23	49	42	61	40	58

E. Velocity

Method 5 calls for the determination of the average velocity of the gas stream by Method 2 for calculation of isokinetic variation. The data from the sampling run are used in the equation:

$$(V_s)_{avg} = 85.48\, C_p\, (\sqrt{\Delta p})_{avg} \sqrt{\frac{(T_s)_{avg}}{P_s M_s}}$$

where

C_p – pitot tube coefficient

$(\sqrt{\Delta p})_{avg}$ – average of the square root of the velocity head

$(T_s)_{avg}$ – average stack temperature

P_s – stack pressure

M_s – molecular weight of the stack gas.

The calculated velocities from the six laboratories that participated in all 13 runs are shown in Table 7. The determinations from the dual trains are not used in order to facilitate blocking the data. In a previous report on Method 2,[7] the precision of the velocity determination was shown to be proportional to the

TABLE 7. DETERMINED VELOCITY OF THE GAS STREAM, ARRANGED BY BLOCK (m/sec)

Run	Labs					
	104	105	106	107	108	109
Block 1						
1	13.9	14.5	15.1	15.4	15.3	14.3
2	13.9	14.4	14.4	14.8	15.5	14.7
7	13.6	14.0	14.8	14.6	15.0	14.4
8	14.3	14.4	14.9	14.8	15.7	14.8
9	14.2	14.3	14.9	15.0	16.2	15.3
Block 2						
3	14.4	14.7	15.8	16.2	16.0	15.7
4	14.2	14.8	15.7	16.0	16.5	16.1
5	14.1	14.3	15.1	15.1	16.2	14.9
6	14.4	14.7	15.4	15.6	15.9	15.2
10	14.5	15.1	15.5	15.5	16.2	14.9
11	14.6	14.9	15.5	15.6	16.6	15.2
12	14.9	15.4	15.9	16.1	16.3	15.3
13	14.8	15.3	15.9	15.9	16.5	15.0

velocity in the range 13 to 18 m/sec. In accordance with this, the precision estimates were made using a coefficient of variation approach, estimating coefficients of variation for the between-laboratory, within-laboratory and laboratory bias terms. The estimates are obtained in Appendix B.5. The model is

$$\beta = \frac{\sigma}{\mu}$$

where

β – the true coefficient of variation

σ – the true standard deviation

and

μ – true mean velocity.

For the purposes of the analysis, the runs are grouped into blocks where the mean velocity is approximately the same for all the runs. The blocking criterion is $(\sqrt{\Delta p})_{avg}$, which is the principal determinant of the velocity. The sample mean of the $(\sqrt{\Delta p})_{avg}$'s is taken across runs, and two blocks are formed. The run averages and the block to which those runs are assigned are given in Table 8.

TABLE 8. BLOCKING CRITERION FOR VELOCITY

Run	$(\sqrt{\Delta\rho})_{avg}$	Block
1	0.64	1
2	0.63	1
3	0.65	2
4	0.67	2
5	0.65	2
6	0.65	2
7	0.63	1
8	0.64	1
9	0.63	1
10	0.66	2
11	0.66	2
12	0.67	2
13	0.66	2

The blocked data were submitted to the coefficient of variation approach described in detail in Appendix B.4. A mean and a standard deviation are calculated for each run across the 6 trains. The ratio of the standard deviation to the mean, multiplied by a correction factor, gives a single estimate of the between-laboratory coefficient of variation, β_b. Averaging the 13 values thus obtained gives

$$\hat{\beta}_b = \frac{1}{13}\sum_{i=1}^{13}\hat{\beta}_i$$

$$= 0.043.$$

There are 5 df associated with this estimate. This gives an estimated standard deviation of

$$\hat{\sigma}_b = \hat{\beta}_b \mu$$

$$= (0.043)\mu$$

or 4.3% of the mean value.

The within-laboratory coefficient of variation is estimated by obtaining a standard deviation and a mean from the velocities obtained by each collaborator with a given block. Since the blocks are of unequal size, the individual beta values are weighted so that a greater contribution is made to the final estimate by the values obtained from the larger numbers of determinations. The weighting procedure is described in Appendix B4.

There are 12 collaborator-block combinations, and the estimated within-laboratory coefficient of variation is

$$\hat{\beta} = \frac{1}{12}\sum_{i=1}^{12}\omega_i\hat{\beta}_i$$

$$= 0.022$$

with 66 df. Thus, the estimated within-laboratory standard deviation is

$$\hat{\sigma} = \hat{\beta}\mu$$

$$= (0.022)\mu,$$

or 2.2% of the mean value.

From these, the laboratory bias coefficient of variation can be estimated as

$$\hat{\beta}_L = \sqrt{\hat{\beta}_b^2 - \hat{\beta}^2}$$

$$= \sqrt{(0.043)^2 - (0.022)^2}$$

$$= \sqrt{(0.0014)}$$

$$= 0.037.$$

This gives an estimated laboratory bias standard deviation of

$$\hat{\sigma}_L = \hat{\beta}_L \mu$$

$$= (0.037)\mu,$$

or 3.7% of the mean value.

In comparison with the previous report, the estimated coefficients of variation were

$$\hat{\beta}_b = 5.0\%$$

$$\hat{\beta} = 3.9\%$$

and

$$\hat{\beta}_L = 3.2\%$$

for between-laboratory, within-laboratory and laboratory bias, respectively. These values compare favorably with those determined in this report, and the conclusion is that a total variation between laboratories of 4 to 5% should be expected.

F. Stack Gas Analysis

Test procedures require that EPA Method 3 be used to determine the stack gas composition and the dry gas molecular weight using an Orsat analyzer or equivalent. All collaborators in this test used Orsat analyzers on an integrated gas sample. The teams operating the paired train analyzed a single gas sample for both trains. The procedures for determining CO_2 and O_2 given in paragraph 4.3.3 of revised Method 3 were strictly adhered to. (Appendix A-2).

There are four missing data points in each set of data. One laboratory did not take Orsats for the first four runs but used the results from the laboratory with which they were paired. Other values within the sets require qualification. One laboratory did not bring the necessary equipment with them to take an integrated sample but performed independent analyses on the gas sample from the other laboratory team on that train. In two other instances, another team's gas sample was used, but independent analyses were

made. These analytical results represent the use of the method with the exception of the collection of the gas sample, where minimum variability would be expected. For this reason, they are retained in the data set for statistical analysis.

Three variables are submitted to statistical analysis to determine the precision of their determination. These are the percent carbon dioxide, percent oxygen, and dry gas molecular weight. The same analysis of variance model is used for each component of interest to determine its precision components.

The data are divided into three analytical sets, one for each week of the test. This is necessitated by the fact that the paired train laboratory changed from week to week. The runs are considered to be repetitions at the same level of each component. The justification for this was a preliminary analysis which showed that the runs were an insignificant factor in the model. The first week has 6 laboratories and three runs, and the next two weeks have 7 laboratories and 5 runs each. The first result in week 2 for laboratory 109 was a replacement value, calculated in the manner described in Snedecor and Cochran.[10] The error term is reduced by 1 degree of freedom as a result.

Precision estimates of the laboratory bias and within-laboratory terms are calculated for each week and then pooled to provide the overall estimates for the method.

1. Percent CO_2

The determinations of the percent CO_2 made by the collaborators are shown in Table 9. The ANOVA tables are shown in Appendix B6. The laboratory term was significant for the second and third weeks, but not the first. The consistently low values for CO_2 by labs 107 and 108 indicate a possible leak in the Orsat Analyzers. As a check on this assumption, the combined $CO_2 + O_2$ values for lab 104 through 109 were examined and not found to be significantly different. This indicates that the low CO_2 values reported were probably due to incomplete CO_2 absorption rather than a system leak.

TABLE 9. PERCENT CO_2 DETERMINATIONS

Run	Labs						
	101	104	105	106*	107	108	109
1	2.8*	2.6	2.6	3.0	2.7	2.5	–†
2	2.7	2.3	2.3	2.0	1.9	2.4	–†
3	3.2	2.6	2.2	2.5	2.0	1.8	–†
	Labs						
	102	104	105	106*	107	108	109
4	2.3*	2.5	2.5	2.6	2.2	1.5	–†
5	2.7	2.6	2.5	2.7	2.4	1.5	2.6
6	2.3	2.6	2.6	2.6	2.0	1.4	2.5
7	2.6	2.2	2.5	2.7	2.4	1.6	2.1
8	2.7	2.3	2.5	2.8	2.2	1.7	2.4
	Labs						
	103	104	105	106*	107	108	109
9	2.5	2.6	2.4	2.6	2.2	1.7	2.3
10	2.8	2.4	2.6	2.7	2.4	1.7	2.6
11	3.1	2.4	2.6	2.5	2.1	2.0	2.4
12	3.1	2.5	2.5	1.8	1.8	2.0	2.6
13	2.7	2.5	2.6	1.9	2.0	2.0	2.5

*Orsat analysis performed on another laboratory's gas sample.
†Orsat analysis not performed.

The three within-laboratory variance estimates were

$$\hat{\sigma}_1^2 = 0.12$$

$$\hat{\sigma}_2^2 = 0.02$$

and

$$\hat{\sigma}_3^2 = 0.05$$

with 12, 27 and 28 df, respectively. Pooling these gives an estimated within-laboratory variance of

$$\hat{\sigma}^2 = 0.04$$

with 67 df. The within-laboratory standard deviation, then is

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= \sqrt{0.04}$$

$$= 0.20 \text{ percent } CO_2.$$

The estimated laboratory bias terms for the two weeks are

$$\hat{\sigma}_{L_2}^2 = 0.14$$

and

$$\hat{\sigma}_{L_3}^2 = 0.09.$$

Combining these gives

$$\hat{\sigma}_L^{\,2} = 0.12$$

with 6 df. This results in a laboratory bias standard deviation of

$$\hat{\sigma}_L = \sqrt{0.12}$$

$$= 0.35 \text{ percent } CO_2 .$$

The between-laboratory variance is estimated from the above to be

$$\hat{\sigma}_b^2 = \hat{\sigma}^2 + \hat{\sigma}_L^2$$

$$= 0.04 + 0.12$$

$$= 0.16$$

with 6 df from the laboratory bias term. The between-laboratory standard deviation, then, is

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}_b^2}$$

$$= \sqrt{0.16}$$

$$= 0.40 \text{ percent } CO_2 .$$

In a previous report,[6] the estimated standard deviations were 1.44, 1.06 and 1.78 percent CO_2 for within-laboratory, laboratory bias and between-laboratory, respectively. The CO_2 levels in that study were considerably higher, however, ranging from 5 percent to 12 percent for the three test sites studied. This suggests that the variability may be a function of the concentration of CO_2 in the gas stream.

To investigate this possibility, the between-laboratory components are examined on a relative basis using the coefficient of variation. For this test, the coefficient of variation is estimated to be

$$\hat{\beta}_b = \frac{\hat{\sigma}_b}{\overline{X}} \times 100\%$$

$$= \frac{0.40}{2.4} \times 100\%$$

$$= 16.7\%$$

For the previous report's data, the overall mean is approximately 9.5 percent CO_2. This gives an estimated coefficient of variation of

$$\hat{\beta}_b = \frac{\hat{\sigma}_b}{\overline{X}} \times 100\%$$

$$= \frac{1.78}{9.5} \times 100\%$$

$$= 18.7\%$$

close to that for this test. The indication is that if this is the proper model for the CO_2 determination, one could expect the CO_2 variation to be between 15% and 20% of the mean concentration.

2. Percent O_2

The determinations of O_2 content in the stack gas are shown in Table 10. These are analyzed under the same model as the CO_2's, and the ANOVA tables and discussion are presented in Appendix B.6. The laboratory term was significant in all three weeks of testing.

TABLE 10. PERCENT O_2 DETERMINATIONS

Run	Labs						
	103	104	105	106*	107	108	109
1	17.7*	17.8	17.9	17.2	18.1	18.5	–†
2	17.9	17.7	18.2	18.1	18.3	18.6	–†
3	17.5	17.7	18.3	17.6	17.6	19.5	–†
	Labs						
	102	104	105	106*	107	108	109
4	18.4*	17.7	18.0	18.0	18.4	19.2	–†
5	18.1	17.8	18.3	17.4	18.3	19.2	18.2
6	17.7	17.7	17.8	17.6	18.7	19.2	18.2
7	17.8	18.1	17.8	17.4	18.2	19.2	18.1
8	17.6	18.1	18.1	17.1	18.5	19.1	18.0
	Labs						
	103	104	105	106*	107	108	109
9	17.0	17.8	18.2	17.5	18.5	19.5	17.7
10	17.2	17.5	17.9	17.4	18.4	19.1	17.8
11	16.7	17.7	18.0	17.7	18.7	18.6	17.8
12	16.5	17.7	18.0	18.4	19.2	18.8	17.7
13	18.1	17.9	18.1	18.3	19.0	18.7	17.8

*Orsat analysis performed on another laboratory's gas sample.
†Orsat analysis not performed.

The within-laboratory variance estimates from the three cases are

$$\hat{\sigma}_1^2 = 0.12$$

$$\hat{\sigma}_2^2 = 0.06$$

and

$$\hat{\sigma}_3^2 = 0.13$$

with 12, 27 and 28 degrees of freedom, respectively. Pooling these estimates gives

$$\hat{\sigma}^2 = 0.10$$

with 67 df. The estimated within-laboratory standard deviation, then, is

$$\hat{\sigma} = \sqrt{0.10}$$

$$= 0.32 \text{ percent } O_2.$$

The laboratory bias variance is estimated as

$$\hat{\sigma}_{L_1}^2 = 0.14$$

$$\hat{\sigma}_{L_2}^2 = 0.27$$

and

$$\hat{\sigma}_{L_3}^2 = 0.38,$$

respectively, from the three weeks. Combining these gives an estimated laboratory bias term of

$$\hat{\sigma}_L^2 = 0.27$$

with 6 df. The laboratory bias standard deviation is estimated as

$$\hat{\sigma}_L = \sqrt{0.27}$$

$$= 0.52 \text{ percent } O_2.$$

The between-laboratory variance is estimated from the above terms as

$$\hat{\sigma}_b^2 = \hat{\sigma}^2 + \hat{\sigma}_L^2$$

$$= 0.10 + 0.27$$

$$= 0.37.$$

This gives an estimated between-laboratory standard deviation of

$$\hat{\sigma}_b = \sqrt{0.37}$$

$$= 0.61 \text{ percent } O_2.$$

In the previous report,[6] the standard deviations were estimated to be 1.70, 1.66 and 2.14 percent O_2 for the within-laboratory, between-laboratory and laboratory bias terms, respectively. As in the case of the CO_2 results, these are larger than the estimates obtained here. The oxygen concentration at the previous sites were lower, however. The variability in O_2 determination appears to be more nearly related to the variability in CO_2 determination than to the O_2 content of the gas stream. There is an apparent trade-off between CO_2 and O_2 determinations that causes their precision to be related to one another. This result would not be unexpected, since any CO_2 not absorbed in the first burette in the Orsat Analyser would be absorbed in the second burette, leading to an increased O_2 value.

3. Molecular Weight

The dry gas molecular weight (Md) is determined from the results of the Orsat analysis. The values obtained for Md in this test are shown in Table 11. In Appendix B.6, the ANOVA tables are presented and the precision estimates derived.

TABLE 11. DRY GAS MOLECULAR WEIGHT DETERMINATIONS (gm/gm-mole)

Run	Labs						
	101	104	105	106*	107	108	109
1	29.16*	29.13	29.13	29.17	29.16	29.14	–†
2	29.14	29.08	29.10	29.04	29.04	29.13	–†
3	29.21	29.12	29.08	29.10	29.02	29.06	–†
	Labs						
	102	104	105	106*	107	108	109
4	29.10*	29.11	29.12	29.14	29.09	29.01	–†
5	29.16	29.13	29.12	29.13	29.12	29.00	29.14
6	29.08	29.12	29.13	29.12	29.07	28.99	29.13
7	29.13	29.07	29.13	29.13	29.11	29.02	28.06
8	29.14	29.09	29.13	29.13	29.09	29.04	29.10
	Labs						
	103	104	105	106*	107	108	109
9	29.08	29.13	29.11	29.12	29.09	29.05	29.08
10	29.13	29.09	29.13	29.13	29.12	29.04	29.13
11	29.16	29.10	29.13	29.10	29.08	29.06	29.10
12	29.15	29.11	29.12	29.03	29.06	29.08	29.12
13	29.16	29.12	29.14	29.04	29.08	29.07	29.11

*Calculated using Orsat analysis on another laboratory's gas sample.
†Orsat analysis not performed.

The within-laboratory variance is estimated to be

$$\hat{\sigma}_1^2 = 0.0024$$

$$\hat{\sigma}_2^2 = 0.0005$$

and

$$\hat{\sigma}_3^2 = 0.0007$$

for the three weeks. There are 12, 27 and 28 df associated with these estimates, respectively. Pooling these gives an overall estimate of

$$\hat{\sigma}^2 = 0.0012$$

with 67 df. The estimated within-laboratory standard deviation, then, is

$$\hat{\sigma} = \sqrt{0.0012}$$

$$= 0.035 \text{ gm/gm-mole}.$$

The labs term was significant for weeks 2 and 3 of the test. The laboratory bias variance estimates are

$$\hat{\sigma}_{L_2}^2 = 0.0015$$

and

$$\hat{\sigma}_{L_3}^2 = 0.0006.$$

Combining these gives an estimated laboratory bias variance of

$$\hat{\sigma}_L^2 = 0.0011$$

with 6 df. The estimated laboratory bias standard deviation is

$$\hat{\sigma}_L = \sqrt{0.0011}$$

$$= 0.033 \text{ gm/gm-mole.}$$

The between-laboratory variance, $\hat{\sigma}_b^2$, is estimated from the above as

$$\hat{\sigma}_b^2 = \hat{\sigma}^2 + \hat{\sigma}_L^2$$

$$= 0.0012 + 0.0011$$

$$= 0.0023,$$

with 6 df. The between-laboratory standard deviation is estimated to be

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}_b^2}$$

$$= \sqrt{0.0023}$$

$$= 0.048 \text{ gm/gm-mole}$$

with 6 df.

The estimates for the previous study[6] were 0.20, 0.14 and 0.24 gm/gm-mole for within-laboratory, laboratory bias and between-laboratory, respectively. The greater imprecision in the previous report's results is undoubtedly due to the greater variation in the CO_2 and O_2 values used to determine Md.

G. Moisture Fraction

Included in the revised Method 5 is a provision for the fraction of moisture in the stack gas to be calculated. The formula is

$$B_{ws} = \frac{V_{w\,\text{std}}}{V_{m\,\text{std}} + V_{w\,\text{std}}}$$

where

B_{ws} – moisture fraction

$V_{w\,\text{std}}$ –volume of water vapor collected, corrected to standard conditions

$V_{m\,\text{std}}$ – metered volume of gas, corrected to standard conditions.

The moisture fractions determined during the test are shown in Table 12 for the eight trains. These are submitted to statistical analysis using an ANOVA model. A two-way model without interaction is used to avoid blocking the runs, and the run-by-train interaction is used for the error term. The details of the analysis are given in Appendix B.7.

TABLE 12. DETERMINED MOISTURE FRACTIONS

Run	Labs							
	101A	101B	104	105	106	107	108	109
1	0.155	0.155	0.160	0.117	0.155	0.145	0.139	0.155
2	0.151	0.156	0.149	0.146	0.148	0.174	0.156	0.154
3	0.172	0.176	0.165	0.141	0.164	0.174	0.164	0.173
	Labs							
	102A	102B	104	105	106	107	108	109
4	0.169	0.175	0.169	0.140	0.174	0.150	0.180	0.174
5	0.138	0.142	0.152	0.151	0.152	0.158	0.158	0.153
6	0.163	0.159	0.158	0.157	0.156	0.148	0.158	0.162
7	0.144	0.144	0.177	0.151	0.144	0.156	0.152	0.152
8	0.152	0.156	0.163	0.162	0.150	0.135	0.157	0.162
	Labs							
	103A	103B	104	105	106	107	108	109
9	0.129	0.135	0.142	0.137	0.130	0.168	0.131	0.136
10	0.169	0.170	0.165	0.158	0.166	0.145	0.168	0.168
11	0.172	0.172	0.165	0.165	0.167	0.172	0.173	0.175
12	0.162	0.164	0.165	0.155	0.156	0.163	0.163	0.162
13	0.149	0.155	0.159	0.147	0.153	0.150	0.154	0.152

The three weeks are analyzed separately, and the run term is significant in each analysis. The estimated within-laboratory variance, σ^2, is

$$\hat{\sigma}_1^2 = 0.000070$$

$$\hat{\sigma}_2^2 = 0.000086$$

and

$$\hat{\sigma}_3^2 = 0.000060$$

from weeks 1, 2 and 3. There are 14, 28 and 28 df, respectively, associated with these estimates. Pooling these terms gives

$$\hat{\sigma}^2 = 0.000073$$

and an estimated within-laboratory standard deviation of

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= 0.009.$$

There are 70 df associated with the pooled estimate.

The trains factor was significant only for the first week's data. The estimated laboratory bias variance is

$$\hat{\sigma}_L^2 = 0.000064$$

with 7 df. This gives a laboratory bias standard deviation estimate of

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}_L^2}$$

$$= 0.008.$$

The between-laboratory variance, σ_b^2, is estimated to be

$$\hat{\sigma}_b^2 = \hat{\sigma}^2 + \hat{\sigma}_L^2$$

$$= 0.000072 + 0.000064$$

$$= 0.000136.$$

The estimated between-laboratory standard deviation, then, is

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}_b^2}$$

$$= \sqrt{0.000136}$$

$$= 0.012.$$

There are 7 df associated with this term, from the laboratory bias component.

In a previous report, the precision components for moisture fraction determination were estimated to be

$$\hat{\sigma} = 0.032$$

$$\hat{\sigma}_L = 0.032$$

and

$$\hat{\sigma}_b = 0.045.$$

In the prior report,[6] the absence of several values from the data set necessitated using runs as repetitions, and undoubtedly caused the error term to be inflated due to run-to-run variation in stack moisture. The higher precision estimates also may result from the higher moisture content of some of the streams sampled to obtain the prior estimates.

H. Precision of Particulate Loadings Corrected to 12% CO_2

The standard for particulate matter emissions from municipal incinerators is given in terms of particulate loading corrected to 12 percent CO_2. To obtain this value, the factor

$$k = \frac{12}{\%CO_2}$$

is applied, where $\%CO_2$ is obtained from the Method 3 results. Thus the standardized concentration, C', is

$$C' = k \cdot C$$

where C is the determined Method 5 concentration. To evaluate the use of these EPA Methods in obtaining a compliance test result, the collaborators' data are used to obtain corrected concentrations, and these are submitted to statistical analysis in the same manner as the uncorrected concentration determinations. The corrected concentrations are shown in Table 13, while the statistical analysis is discussed in detail in Appendix B8. The within-laboratory variance is estimated from the difference between the two trains run by a single laboratory. The estimates obtained are summarized in Table 14. Using Bartlett's test, the three MS's can be shown to be estimating the same true variance, σ^2, at a 5% significance level. Thus, the best estimate of the within-laboratory variance is obtained from the pooled estimate, giving

$$\hat{\sigma}^2 = 3072.88$$

with 13 df.

TABLE 13. PARTICULATE CONCENTRATION CORRECTED TO 12% CO_2, mg/scm

Run	Labs											
	101		102		103		104	105	106	107	108	109
	A	B	A	B	A	B						
1	505.3	568.3					874.6	564.5	556.0	612.4	649.0	605.8
2	448.0	471.6					677.7	414.3	600.6	554.5	615.0	518.0
3	481.9	508.9					664.2	736.4	597.1	700.2	675.3	714.0
4			751.8	772.7			747.8	724.8	658.2	739.6	1132.8	988.0
5			459.6	499.1			555.2	598.6	492.0	536.0	952.8	570.5
6			787.3	695.5			689.1	569.1	672.5	710.5	1513.7	767.5
7			378.0	377.1			552.0	621.1	405.3	431.0	744.8	469.7
8			450.2	463.1			715.8	547.7	513.9	637.6	989.7	479.5
9					485.8	516.5	449.5	518.9	433.8	486.6	668.5	470.6
10					674.1	677.6	790.5	665.5	650.7	700.5	961.4	792.9
11					657.7*	624.4	814.0	574.2	756.5	886.3	1064.4	764.0
12					985.2	736.3	787.7	704.2	1013.3	987.3	928.2	636.0
13					838.2	844.0	888.5	726.5	1007.4	928.2	982.8	667.7

*Substituted value.

TABLE 14. PRECISION ESTIMATION BETWEEN PAIRED-TRAIN LABORATORIES
(Particulate Concentration Corrected to 12% CO_2)

Lab	SS	df	MS	$\hat{\sigma}$	$\hat{\beta}$, %
101	2.627.48	3	875.83	29.59	5.0
102	5.295.76	5	1.059.15	32.54	4.9
103	32.024.20	5	6.404.84	80.03	10.8
Pooled	39.947.44	13	3.072.88	55.43	8.2

The estimated within-laboratory standard deviation, then, is

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= \sqrt{3072.88}$$

= 55.43 mg/scm, corrected to 12% CO_2.

The coefficient of variation is estimated using the overall mean of 677.13, giving,

$$\hat{\beta} = \hat{\sigma}/\hat{\mu}$$

$$= 55.43/677.13$$

$$= 0.082$$

or 8.2 percent of the mean level.

If the ordinary error term from the ANOVA were to be used, the pooled estimate of σ would be

$$\hat{\sigma} = 96.52 \text{ mg/scm}$$

corrected to 12% CO_2 and the estimated coefficient of variation would be

$$\hat{\beta} = 0.143$$

or 14.3% of the mean value. The discrepancy between the two probably results from the fact that, in the paired-train laboratories' results, there is no additional variation induced by the Orsat data, since a single sample was taken for both trains. From run to run by the same laboratory, however, there is apparently some additional error due to the determined CO_2 concentration.

The laboratory bias variance is estimated from the contrasts between paired laboratories, as before. The pooled laboratory mean square is 174,868.84. Using the EMS of this term, the estimated laboratory bias variance is

$$\hat{\sigma}_L^2 = 13{,}215.07,$$

with 3 df. The estimated laboratory bias standard deviation, then, is

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}_L^2}$$

$$= 114.96 \text{ mg/scm, corrected to 12\% } CO_2.$$

The estimated coefficient of variation is

$$\hat{\beta}_L = \hat{\sigma}_L / \hat{\mu}$$

$$= 114.96/677.13$$

$$= 0.170$$

or 17.0% of the mean value.

The between-laboratory component, σ_b^2, is estimated from the above as

$$\hat{\sigma}_b^2 = \hat{\sigma} + \hat{\sigma}_L^2$$

$$= 3072.88 + 13{,}215.07$$

$$= 16{,}287.95.$$

This gives an estimated between-laboratory standard deviation of

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}_b^2}$$

$$= 127.62 \text{ mg/scm, corrected to 12\% } CO_2$$

with 3 df, from the laboratory bias term. In terms of relative variation, then, the coefficient of variation is estimated to be

$$\hat{\beta} = \frac{\hat{\sigma}_b}{\hat{\mu}}$$

$$= \frac{127.62}{677.13}$$

$$= 0.188,$$

or 18.8% of the mean value.

If the alternative within-laboratory term were to be used, the one which takes the run to run variation in CO_2 determination into account, the between-laboratory components would be

$$\hat{\sigma}_b^2 = 22{,}530.29$$

$$\hat{\sigma}_b = 150.10$$

and

$$\hat{\beta}_b = 0.222$$

Thus, the concentrations from lab to lab would be expected to have a standard variation, in relative terms, of 22.2% of the mean value.

In comparison to the results for a Method 5 concentration determination, it can be seen that, using the paired train laboratory's results, the within-laboratory relative variation dropped slightly, while the laboratory bias increased greatly. Also, there was an increase in the relative variation of the error term taken from the ANOVA. This increase is due to variation in the CO_2 determination from the Orsat data. The between-laboratory standard deviation for CO_2 is 0.40 percent CO_2 by volume. If the true CO_2 level were 2.3 percent, then two independent laboratories might obtain values of 2.1 percent and 2.5 percent, respectively. For two laboratories which had determined the same concentration, C, the corrected concentrations would be

$$C'_1 = \left(\frac{12}{2.1}\right)C$$

and

$$C'_2 = \left(\frac{12}{2.5}\right)C$$

and as a result

$$C'_1/C'_2 = 1.19,$$

or a 19% difference would be induced.

IV. COMPARISON WITH PREVIOUS STUDIES

The results from the evaluation of Method 5 can be compared to the results of the three previous studies. In these studies, the precision components were estimated in terms of coefficients of variation, and these are summarized in Table 15, along with the estimated coefficients of variation from this study.

TABLE 15. COMPARISON OF COEFFICIENTS OF VARIATION FOR METHOD 5

Site	Coefficients of Variation, %		
	Within-Laboratory	Laboratory Bias	Between-Laboratory
Portland Cement Plant	28.4	51.0	58.4
(after high values excluded)	9.8	17.6	20.1
Power Plant	31.1	19.5	36.7
Houston Incinerator	25.3	29.3	38.7
Dade County Incinerator	10.4	6.1	12.1

It is easily seen that the estimates for this test are considerably lower than those from the previous studies, and there are several possible reasons for this. First, the purpose of this test was to determine the minimum variability that could be expected with the use of Method 5. To accomplish this, the collaborators were chosen from laboratories who had a great deal of experience using Method 5, and who had been under contract to EPA for source testing. In previous studies, the laboratories were chosen from professional source samplers in the local area in which the testing was conducted, since they were deemed representative of source samplers in general. The calibration checks and rechecks required for this test were not specified in previous tests except to the extent that they were required in proper use of the method. By these checks, some of the laboratory-to-laboratory differences could be eliminated, as in the case of the laboratories whose meter boxes were out of calibration upon arrival at the test site.

Secondly, in all previous studies, the authors had urged that the procedural details in the method be tightened and more well-defined. It was felt, and is still felt, that differences from one crew to another in the manner of handling these procedural details were the greatest single source of variation between laboratories. In the revised Method 5 shown in Appendix A3, the sample handling and recovery is defined more precisely, and teams who follow the new method scrupulously should be able to obtain more reproducible results.

In addition, the statistical analyses of the previous studies' data were hampered by results that could not be used because of failure to meet either the minimum sampling volume or isokinetic variation criteria. In this study, only one data point was deemed invalid, where a broken probe liner and contaminated filter were noted after the run. After substituting for this value, a more valid error estimate was obtainable since it was no longer necessary to perform some type of posterior blocking of the data to obtain a within-laboratory term. Also, the laboratory bias term was based upon 6 observations per run, instead of the maximum 4, and often as few as 2 or 3 per run in the previous tests. This has to give a better estimate, and one which is affected less by an extremely high or low value.

APPENDIX A. REVISED EPA METHODS FOR PARTICULATE EMISSION MEASUREMENT

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APPENDIX A

A1. Method 2—Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)

1. Principle and Applicability

1.1 Principle. Stack gas velocity is determined from the gas density and from measurement of the velocity head using a Type S (Stausscheibe or reverse type) pitot tube.

1.2 Applicability. This method should be applied only when specified by the test procedures for determining compliance with the new source performance standards.

This procedure is not applicable for direct measurement in cyclonic or swirling gas streams. (Method 1, section 2.4 shows how to determine unacceptable flow conditions.) When these conditions exist, procedures such as the use of flow straightening devices must be employed as necessary to make accurate flow rate determinations. Such procedures are subject to approval by the Administrator.

2. Apparatus

Specifications for the apparatus are given below. Any apparatus which has been demonstrated to the Administrator's satisfaction to be capable of meeting the specifications will be considered acceptable for the purposes of this method.

2.1 Pitot tube. Type S (Figure 2-1), or equivalent, calibrated according to the procedure in section 4. Other devices may be used when approved by the Administrator.

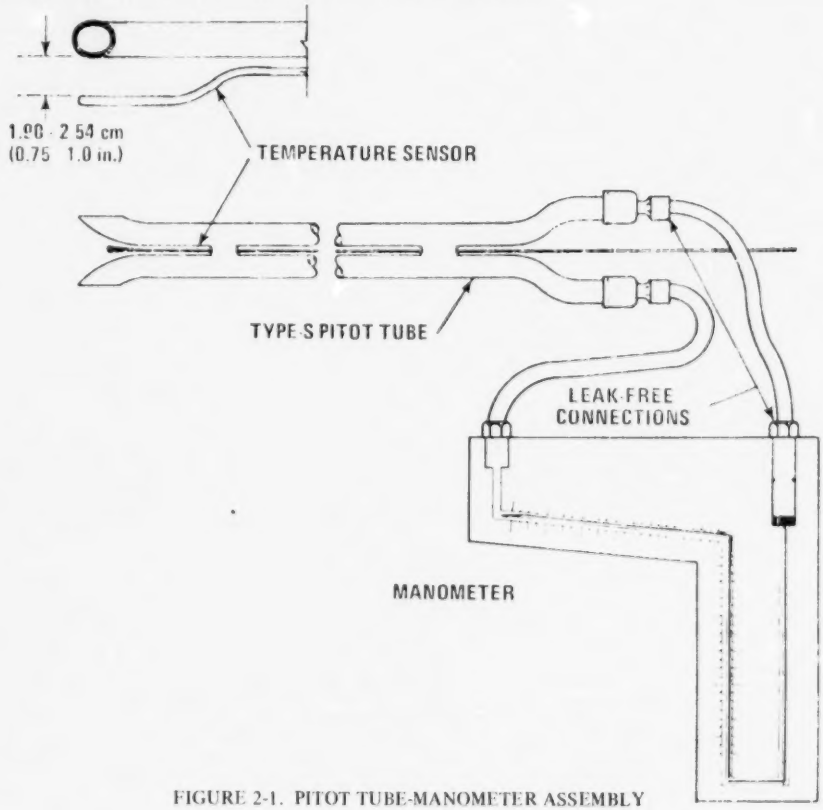

FIGURE 2-1. PITOT TUBE-MANOMETER ASSEMBLY

2.2 Differential pressure gauge. Inclined manometer, or equivalent device, capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, methods or other devices acceptable to the Administrator may be used when conditions warrant.

2.3 Temperature gauge. Thermocouple, liquid filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauges that are capable of measuring temperature to within 1.5% of the minimum absolute stack temperature. The temperature gauge shall be attached to the pitot tube such that the sensor does not touch any metal and its position is adjacent and about 1.90 to 2.54 cm (0.75 to 1 in.) from the pitot tube openings (see Figure 2-1). If it can be shown to the satisfaction of the Administrator that a difference of not more than 1% in the velocity measurement will be introduced, the temperature gauge need not be attached to the pitot tube.

2.4 Pressure probe and gauge. Piezometer tube and mercury-or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm Hg (0.1 in. Hg). The static tap of a standard type pitot tube or one leg of a Type S pitot tube with the face openings positioned parallel to the gas flow may also be used as the pressure probe.

2.5 Barometer. Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

2.6 Gas analyzer. To analyze gas composition for determining molecular weight. Use Method 3 or other methods specified by the Administrator for dry molecular weight and use Method 5 or Reference Method 4 for moisture content. Other methods may be used when approved by the Administrator.

2.7 Calibration pitot tube. Standard type, to calibrate the Type S pitot tube. The standard type pitot tube shall have a known coefficient obtained from the National Bureau of Standards, Route 70 S, Quince Orchard Road, Gaithersburg, Maryland. An alternative is to use a Prandtl type pitot tube designed according to the criteria (given below and illustrated in Figure 2-2) which ensure that its coefficient will be 0.99 ± 0.01.

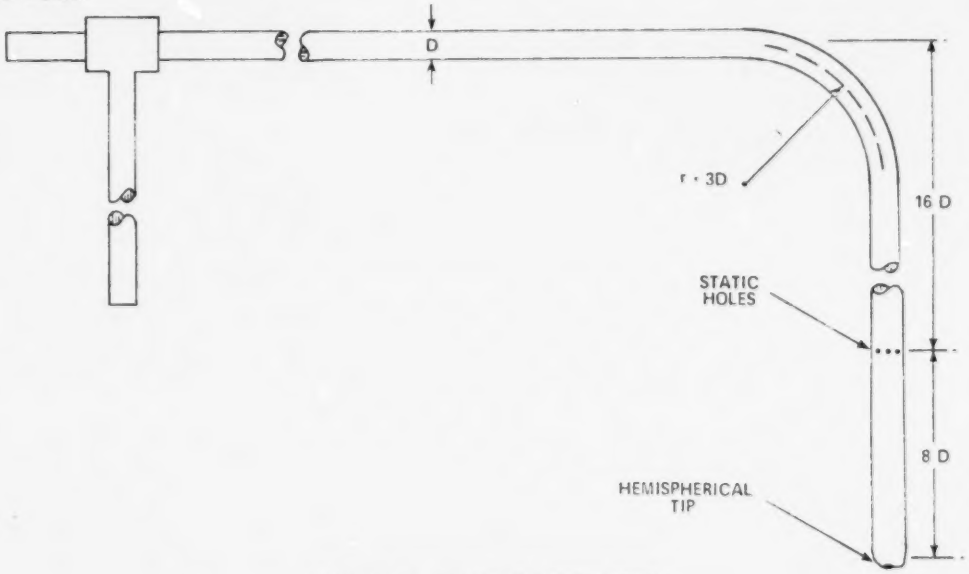

FIGURE 2-2. STANDARD PITOT TUBE

2.7.1 Hemispherical tip (inlet end of the impact tube).

2.7.2 Eight diameters of straight run (based on the diameter of the external tube) between the tip and the static pressure holes.

2.7.3 Sixteen diameters between the static pressure holes and the centerline of the external tube, following the 90° bend.

2.7.4 Eight static pressure holes of equal size (approximately 1/32 in. diameter), equally spaced in a piezometer ring configuration.

2.7.5 Ninety-degree bend of relatively large radius (approximately three diameters).

2.8 Calibration differential pressure gauge. For calibration purposes, inclined manometer, or equivalent device, capable of measuring velocity head to within 0.13 mm H_2O (0.005 in. H_2O).

3. Procedure

3.1 Set up the apparatus as shown in Figure 2-1. Make sure all connections are tight and leak free. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the sample run. Record all necessary data as shown in the example data sheet (Figure 2-3).

3.2 Measure the velocity head and temperature at the traverse points specified by Method 1.

3.3 Measure the static pressure in the stack. One reading is usually adequate for all measuring points during the test; however, this must be confirmed by randomly moving the pressure probe over the cross section to see if there are any significant variations, i.e., greater than about 100 mm H_2O (4 in. H_2O). If there are significant variations, check the location for disturbances. If none are found, measure and record the static pressure at each traverse point.

3.4 Determine the atmospheric pressure.

3.5 Determine the dry stack gas molecular weight. For combustion processes, use Method 3. For processes emitting essentially air, an analysis need not be conducted; use a molecular weight of 29. For other processes, consult the Administrator.

3.6 Obtain the moisture content from Method 5 or by using Reference Method 4.

3.7 Determine the cross sectional area of the stack or duct at the sampling location.

4. Calibration

4.1 Pitot tube.

4.1.1 Calibration set-up. Calibration shall be done in a flow system having the following essential design features:

4.1.1.1 The "flowing gas stream" must be confined to a definite cross sectional area, either circular or rectangular. The projected area of the pitot tube (area exposed to the gas stream and perpendicular to the direction of flow) shall be less than 2% of the duct cross sectional area. Assuming a 0.95 cm (3/8 in.) diameter pitot tube and a measuring point at the centroid, the diameter of a circular duct must be at least 30.5 cm (12 in.) and the width (shorter side) of a rectangular duct must be at least 30.5 cm (12 in.). If the pitot tube is to be calibrated with a particulate probe sheath attached, as in Method 5, larger cross sections must be employed to meet the 2% criterion.

PLANT _____

DATE _____ RUN NO. _____

STACK DIAMETER OR DIMENSIONS, m(in.) _____

BAROMETRIC PRESSURE, mm Hg (in. Hg) _____

CROSS SECTIONAL AREA, $m^2(ft^2)$ _____

OPERATORS _____

PITOT TUBE I.D. NO. _____

AVG. COEFFICIENT, C_p = _____

LAST DATE CALIBRATED _____

SCHEMATIC OF STACK CROSS SECTION

Traverse Pt. No.	Vel. Hd., Δp mm (in.) H_2O	Stack Temperature		P_g[a] mm Hg (in.Hg)	$\sqrt{\Delta p}$
		t_s, °C (°F)	T_s, °K (°R)		

The cross sectional area must be constant over a distance of 10 or more duct diameters. For a rectangular cross section, use an equivalent diameter calculated from the following equation to determine the number of duct diameters:

$$D_e = \frac{2\,L\,W}{(L + W)} \qquad \text{Equation 2-1}$$

where:

D_e = equivalent diameter

L = length

W = width

4.1.1.2 To ensure the presence of stable, fully developed flow patterns at the calibration site, or "test section," the site must be located at least 8 diameters downstream and two diameters upstream from the nearest disturbances.

4.1.1.3 The system must have the capacity to generate a test section velocity of at least 600 m/min (2000 fpm). The velocity must be constant with time, to guarantee the presence of steady flow during calibration.

4.1.1.4 Two entry ports, one each for the standard and Type S pitot tubes, shall be cut in the test section; the standard pitot entry port shall be located slightly downstream of the Type S port, so that the standard and Type S impact openings will lie in the same plane during calibration. To facilitate alignment of the pitot tubes during calibration, it is advisable that the test section be constructed of plexiglas or some other transparent material.

4.1.2 Calibration procedure. It is recommended that an identification number be assigned to the pitot tube, and that this number be permanently marked or engraved on the body of the tube; also, one leg of the tube should be marked "A", and the other, "B". To obtain calibration data for both the "A" and "B" sides, proceed as follows:

4.1.2.1 Clean and fill the manometer. Inspect and leak check all pitot lines and fittings; repair or replace if necessary.

4.1.2.2 Level and zero the manometer. Turn on the fan and allow the flow to stabilize. Seal with tape the Type S entry port.

4.1.2.3 Using the standard type pitot tube, locate an area where there is little or no velocity variation over a 5 cm (2 in.) square segment.

4.1.2.4 Ensure that the manometer is level and zeroed. Then position the standard pitot tube within the area determined in section 4.1.2.3 and align it so that its tip is pointing directly into the flow; particular care should be taken to avoid "yaw" and "pitch" angles. Make sure that the entry port surrounding the tube is properly sealed.

4.1.2.5 Read Δp_{std} and record its value in a data table similar to that shown in Figure 2-4. Remove the standard pitot tube from the duct; disconnect it from the manometer.

4.1.2.6 Seal the standard port and open the Type S port. Connect the Type S tube to the manometer. Check the manometer level and zero. Insert and align the Type S pitot tube so that the "A" side impact opening is at the same measuring point (within the area determined in section 4.1.2.3) as was the standard

PITOT TUBE IDENTIFICATION NUMBER: _____ DATE: _____

CALIBRATED BY: _____

"A" SIDE CALIBRATION				
RUN NO.	Δp_{std} cm H_2O (in. H_2O)	$\Delta p_{(s)}$ cm H_2O (in. H_2O)	$C_{p(S)}$	DEV.
1				
2				
3				
		AVERAGE		

"B" SIDE CALIBRATION"				
RUN NO.	Δp_{std} cm H_2O (in. H_2O)	$\Delta p_{(s)}$ cm H_2O (in. H_2O)	$C_{p(S)}$	DEV.
1				
2				
3				
		AVERAGE		

DEV. = $\frac{C_{p(S)} - C_{p(S)(avg.)}}{C_{p(S)(avg.)}}$ (MUST BE ≤ 0.01)

C_p DIFFERENCE: $A_{avg} - B_{avg}$ = _____ (MUST BE $\leq$ 0.01)

FIGURE 2-4. PITOT TUBE CALIBRATION DATA

tube and is pointing directly into the flow. Make sure that the entry port surrounding the tube is properly sealed.

4.1.2.7 Read Δp_S and record its value in the data table. Remove the Type S tube from the duct and disconnect the manometer.

4.1.2.8 Repeat steps 4.1.2.4 through 4.1.2.7 above until three sets of velocity head measurements yield $C_{p(S)}$ values (calculated from Equation 2-2) that agree to within 0.01 of their average.

4.1.2.9 Repeat steps 4.1.2.4 through 4.1.2.8 for the "B" side.

4.1.3 Calculations.

4.1.3.1 For each data point, calculate the Type S pitot tube coefficient using the following formula:

$$C_{p(S)} = C_{p(std)} \sqrt{\frac{\Delta p_{std}}{\Delta p_S}} \qquad \text{Equation 2-2}$$

where:

$C_{p(S)}$ = Type S pitot tube coefficient.

$C_{p(std)}$ = Standard pitot tube coefficient; use 0.99 if the coefficient is unknown and the tube is designed according to the guidelines in section 2.7.

Δp_{std} = Velocity head measured by the standard pitot tube, cm H_2O (in. H_2O).

Δp_S = Velocity head measured by the Type S pitot tube, cm H_2O (in. H_2O).

4.1.3.2 Determine the average C_p for side "A" and likewise for side "B"; determine the difference between these two average values. Use the pitot tube only if the difference in C_p's is no more than 0.01. Greater values indicate improperly constructed pitot tubes.

4.1.3.3 Depending on direction in which the pitot tube is faced, use corresponding average C_p for velocity calculations.

4.1.4 Frequency of Calibration and Maintenance. Each pitot tube shall be calibrated before initial use. Thereafter, if the tube has been significantly damaged by field use, i.e., if impact faces are badly bent out of shape, cut, nicked, or noticeably misaligned, the tube shall be repaired and recalibrated, or replaced.

4.2 Temperature gauges. Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. New thermocouples need not be calibrated. Calibrate used thermocouples against new ones. For other devices, check with the Administrator.

4.3 Barometers. Calibrate against a mercury barometer.

5. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

5.1 Nomenclature.

A = Cross sectional area of stack, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream (from Method 5 or Reference Method 4), proportion by volume.

C_p = Pitot tube coefficient, dimensionless.

K_p = Pitot tube constant, $34.97 \frac{m}{sec}\left[\frac{(g/g\text{-mole})(mm\ Hg)}{(^\circ K)(mm\ H_2O)}\right]^{1/2}$ for the metric system and

$85.48 \frac{ft}{sec}\left[\frac{(lb/lb\text{-mole})(in.\ Hg)}{(^\circ R)(in.\ H_2O)}\right]^{1/2}$ for the English system.

M_d = Molecular weight of stack gas, dry basis (from Method 3 or other approved methods), g/g-mole (lb/lb-mole).

M_s = Molecular weight of stack gas, wet basis, g/g-mole (lb/lb-mole).

$= M_d(1 - B_{ws}) + 18\,B_{ws}$ Equation 2-3

P_{bar} = Atmospheric pressure, mm Hg (in. Hg).

P_g = Stack static pressure, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

$= P_{bar} + P_g$ Equation 2-4

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{sd} = Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).

t_s = Stack temperature, °C (°F).

T_s = Absolute stack temperature, °K (°R).

$= 273 + t_s$ for metric Equation 2-5

$= 460 + t_s$ for English Equation 2-6

T_{std} = Standard absolute temperature, 293°K (528°R).

v_s = Average stack gas velocity, m/sec (ft/sec).

Δp = Velocity head of stack gas, mm H_2O (in. H_2O).

3600 = Conversion factor, sec/hr.

18 = Molecular weight of water, g/g-mole (lb/lb-mole).

5.2 Average stack gas velocity.

$$v_s = K_p\, C_p\, (\sqrt{\Delta p})_{avg} \sqrt{\frac{(T_s)_{avg}}{P_s M_s}} \qquad \text{Equation 2-7}$$

Note: Equation 2-7 assumes that T_s, P_s, and M_s do not change appreciably (i.e. >1%) with cross section and with time. If they do, consult with the Administrator to determine an acceptable procedure.

5.3 Average stack gas dry volumetric flow rate.

$$Q_{sd} = 3600\,(1 - B_{ws})\, V_s\, A \left[\frac{T_{std}}{T_{s(avg)}}\right]\left[\frac{P_s}{P_{std}}\right] \qquad \text{Equation 2-8}$$

6. References

6.1 Mark, L.S., Mechanical Engineer's Handbook, McGraw-Hill Book Co., Inc., New York, N.Y., 1951.

6.2 Perry, J.H., Chemical Engineers' Handbook, McGraw-Hill Book Co., Inc., New York, N.Y., 1960.

6.3 Shigehara, R.T., W.F. Todd, and W.S. Smith, Significance of Errors in Stack Sampling Measurements. Paper presented at the Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14-19, 1970.

6.4 Standard Method for Sampling Stacks for Particulate Matter. In: 1971 Book of ASTM Standards, Part 23, Philadelphia, Pa., 1971. ASTM Designation D-2928-71.

6.5 Vennard, J.K., Elementary Fluid Mechanics, John Wiley & Sons, Inc., New York, N.Y., 1947.

6.6 ASME, Fluid Meters–Their Theory and Application, ASME, N.Y., 1959.

A2. Method 3—Gas Analysis for Carbon Dioxide, Oxygen, Excess Air and Dry Molecular Weight

1. Principle and Applicability

1.1 Principle. An integrated or grab gas sample is extracted from a stack and analyzed for percent carbon dioxide and percent oxygen using an Orsat analyzer or, for molecular weight determinations, a Fyrite[1] type combustion gas analyzer.

1.2 Applicability. This method should be applied only when specified by the test procedures for determining compliance with the standards of performance for new stationary sources.

2. Apparatus

Any apparatus which has been demonstrated to yield results acceptable to the Administrator will be considered acceptable for the purposes of this method.

2.1 Grab sample (Figure 3-1).

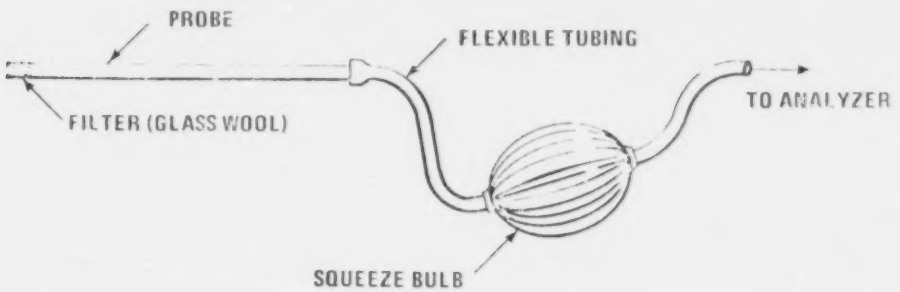

FIGURE 3-1. GRAB-SAMPLING TRAIN

2.1.1 Probe. Stainless steel or borosilicate glass equipped with a filter (either in-stack or out-stack) to remove particulate matter.

2.1.2 Pump. One-way squeeze bulb, or equivalent, to transport gas sample to analyzer.

2.2 Integrated sample (Figure 3-2).

2.2.1 Probe. Stainless steel or borosilicate glass equipped with a filter (either in-stack or out-stack) to remove particulate matter.

2.2.2 Condenser. Air-cooled condenser, or equivalent, to remove excess moisture.

2.2.3 Valve. Needle valve, to adjust sample gas flow rate.

2.2.4 Pump. Leak-free, diaphragm type, or equivalent, to transport sample gas to the flexible bag. Install a small surge tank between the pump and rate meter to eliminate pulsation effect of diaphragm pump on the rotameter.

2.2.5 Rate meter. Rotameter, capable of measuring a flow range from 0 to 1.0 liter per minute.

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

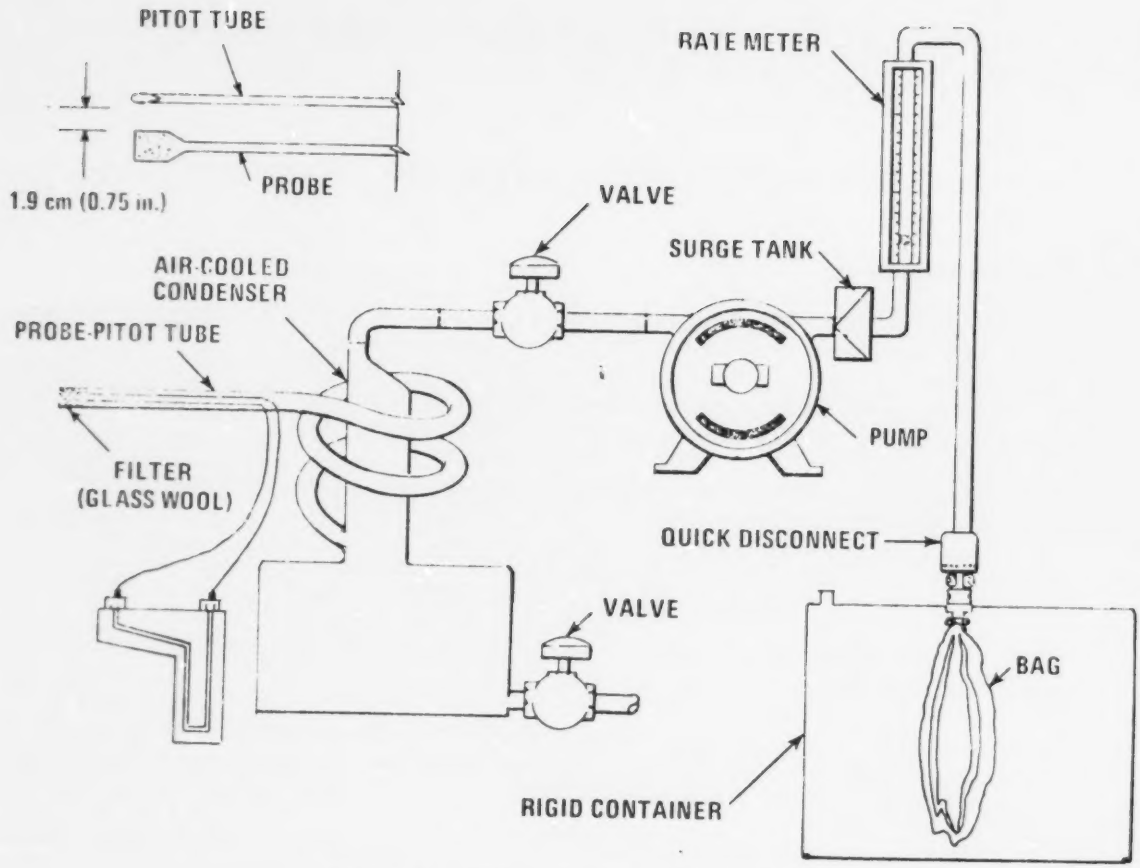


FIGURE 3-2. INTEGRATED GAS-SAMPLING TRAIN

2.2.6 Flexible bag. Tedlar,[1] or equivalent, with a capacity in the range of 55 to 90 liters. Before each field test make sure the bag is leak-free by checking it for leaks. To leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. (Note: An alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.)

2.2.7 Pitot tube. Type S, or equivalent, attached to the probe to allow constant monitoring of the stack gas velocity so that the sampling flow rate can be regulated proportional to the stack gas velocity. The tips of the probe and pitot tube shall be adjacent to each other and the free space between them shall be 1.9 cm (0.75 in.). The pitot tube must also meet the criteria specified in Method 2 and be calibrated according to the procedure in the calibration section of that method.

2.2.8 Differential pressure gauge. Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, methods or other devices acceptable to the Administrator may be used when conditions warrant.

2.2.9 Manometer. About 28 cm (12 in.) water-filled U-tube manometer, or equivalent, to be used for the flexible bag leak check.

2.2.10 Vacuum gauge. At least 760 mm Hg (30 in. Hg) gauge, to be used for the sampling train leak check.

2.3 Analysis

2.3.1 Orsat analyzer or Fyrite[1] type combustion gas analyzer. The latter is used only for molecular weight determination.

3. Sampling Procedure

3.1 Grab sampling. This procedure is primarily used for, but not limited to, determining molecular weight. Other uses must first be approved by the Administrator.

3.1.1 The sampling point in the duct shall be at the centroid of the cross section or at a point no closer to the walls than 1 m (3.28 ft), unless otherwise specified by the Administrator.

3.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections are tight and leak-free by following the procedure in Section 4.

3.1.3 Place the probe in the stack at the sampling point and then purge the sampling line. Draw a sample into the analyzer and analyze according to Section 4.

3.2 Integrated sampling (required when the analytical results will be used to calculate a pollutant emission rate correction factor).

3.2.1 Locate the sampling points according to Method 1, except that a minimum of 12 points shall be used in all cases, unless otherwise specified in an applicable subpart. For circular stacks of less than or equal to 0.6 m (2 ft), a minimum of 8 points shall be used.

Depending on the degree of mixing, more or less points than the above may be used. As a general rule, if the sampling location is located 8 diameters (equivalent diameters) downstream from points of air in-leakages with good mixing (disturbances) in between, one point at the centroid or no closer than 1 m (3.28 ft) from the stack walls may be used. If considerable variation as evidenced by a concentration traverse or by review of the ductwork design and points of air in-leakages, more points in accordance with Method 1 shall be used. The number of diameters shall be calculated using the linear distance from the point of air in-leakage and the diameter of the stack at the sampling location.

3.2.2 Leak check the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak check the train by placing a vacuum gauge at the probe inlet pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum shall remain stable for at least two minutes. Evacuate the flexible bag. Place the probe in the stack and then purge the sampling line. Now, connect the bag and make sure that all connections are tight and leak free.

3.2.3 Sample at a rate proportional (within 20% of constant proportionality, or as specified by the Administrator) to the stack velocity, traversing all sampling points. Record proportional sampling data as shown in Figure 3-3. When analytical results will be used to calculate a pollutant emission rate correction factor, the sampling MUST span the length of time the pollutant emission rate is being determined, sampling at each traverse point for equal length of time. Collect at least 30 liters (1 ft^3) of sample gas.

3.2.4 Obtain and analyze at least one integrated flue gas sample during each pollutant emission rate determination.

TIME	TRAVERSE PT.	Δp mm(in.) H_2O	Q lpm	$R = \frac{Q}{\sqrt{\Delta p}}$	% DEV.[a]
			AVERAGE		

[a] % DEV = $\left(\frac{R - R_{avg}}{R_{avg}}\right) 100$ (MUST BE $\leq$ 20%)

FIGURE 3-3. PROPORTIONAL SAMPLING DATA

4. Analytical Procedure

4.1 Leak check for Orsat analyzer. Moving an Orsat analyzer frequently causes it to leak. Therefore, an Orsat analyzer should be thoroughly leak-checked on-site before the flue gas sample is introduced into it. The suggested procedure for leak-checking an Orsat analyzer is:

4.1.1 Bring the liquid level in each pipette up to the reference mark on the capillary tubing and then close the pipette stopcock.

4.1.2 Raise the leveling bulb sufficiently to bring the confining liquid meniscus onto the graduated portion of the burette and then close the manifold stopcock.

4.1.3 Record the meniscus position.

4.1.4 Observe the meniscus in the burette and the liquid level in the pipette for movement over the next four minutes.

4.1.5 For the Orsat analyzer to pass the leak-check, two conditions must be met:

4.1.5.1 The liquid level in each pipette must not fall below the bottom of the capillary tubing during this four-minute interval.

4.1.5.2 The meniscus in the burette must not change by more than 0.2 ml during this four-minute interval. For the results to be valid the Orsat analyzer must pass this leak test before and after the analysis.

4.1.6 If the analyzer fails the leak-check procedure, all rubber connections and stopcocks should be checked until the cause of the leak is identified. Leaking stopcocks must be disassembled, cleaned and regreased. Leaking rubber connections must be replaced. After the analyzer is reassembled, the leak-check procedure must be repeated.

4.2 Determination of stack gas molecular weight. (Orsat leak check described above is optional). Within eight hours after the sample is taken, analyze it for percent carbon dioxide and percent oxygen using either an Orsat analyzer or a Fyrite[1] type combustion gas analyzer. Determine the percent of the gas that is nitrogen and carbon monoxide by subtracting the sum of the percent carbon dioxide and percent oxygen from 100 percent.

4.2.1 Grab samples. Repeat the sampling and analysis until the molecular weight from each of three consecutive grab samples differs from their mean by no more than 0.3 grams/gram mole (0.3 pounds/pound mole).

4.2.2 Integrated samples. Repeat the analysis until the molecular weight for three consecutive analyses differs from their mean by no more than 0.3 grams/gram mole (0.3 pounds/pound mole).

4.3 Determination of O_2, CO_2, or excess air for calculating pollutant emission rate correction factors. Note: The Fyrite type combustion gas analyzers are not acceptable for this purpose, unless otherwise shown to the satisfaction of the Administrator. The results may also be used for determining stack gas molecular weight.

4.3.1 Leak check the Orsat analyzer as described in section 4.1. This procedure is mandatory.

4.3.2 Within four hours after the integrated sample is taken, analyze it for percent carbon dioxide and percent oxygen using an Orsat analyzer. To ensure complete absorption of these gases make repeated passes through the absorbing solution until two consecutive readings are the same. Several passes (3-4) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.) Determine the percent of the gas that is nitrogen and carbon monoxide by subtracting the sum of the percent carbon dioxide and percent oxygen from 100 percent.

This procedure assumes that carbon monoxide concentration is negligible. If appreciable quantities are expected, consult with the Administrator.

4.3.3 Repeat the analysis on the integrated sample until each of three consecutive analyses for percent carbon dioxide and percent oxygen differ by no more than 0.3 percent by volume when carbon dioxide is greater than 3% and 0.2 percent by volume when carbon dioxide is less than or equal to 3%.

5. Calibration

5.1 Calibrate the pitot tube as specified in Method 2 and the rotameter against a wet test meter.

6. Calculations

6.1 Nomenclature

M_d = Dry molecular weight (gram/gram mole).

%EA = Percent excess air.

$\%CO_2$ = Percent carbon dioxide by volume (dry basis).

$\%O_2$ = Percent oxygen by volume (dry basis).

%N = Percent nitrogen by volume (dry basis).

0.264 = Ratio of oxygen to nitrogen in air, v/v.

0.28 = Molecular weight of both nitrogen and CO divided by 100.

0.32 = Molecular weight of oxygen divided by 100.

0.44 = Molecular weight of carbon dioxide divided by 100.

6.2 Excess air. Use equation 3-1 to calculate the percent excess air using the three consecutive analyses that meet the requirements of section 4.3.3. Then calculate the average percent excess air.

$$\%EA = \frac{\%O_2\ (100)}{0.264\ \%N_2 - \%O_2} \qquad \text{Equation 3-1}$$

Note: The equation above assumes that carbon monoxide concentration is negligible. If appreciable carbon monoxide concentrations are expected, consult with the Administrator.

6.3 Dry molecular weight. Use equation 3-2 to calculate the dry molecular weights using data obtained from sections 4.2.1, 4.2.2, or 4.3.2 and 4.3.3, average the results and report to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

$$M_d = 0.44(\%CO_2) + 0.32(\%O_2) + 0.28(\%N_2 + \%CO) \qquad \text{Equation 3-2}$$

6.4 Carbon dioxide concentration calculation. Using the three consecutive carbon dioxide analyses that meet the requirements of section 4.3.3, calculate the average carbon dioxide concentration.

7. References

7.1 Altshuller, A. P. Storage of Gases and Vapors in Plastic Bags, International Journal of Air and Water Pollution, 6, 75-81 (1963).

7.2 Connor, William D. and J. S. Nader, Air Sampling with Plastic Bags, Journal of the American Industrial Hygiene Association, 25, 291-297 (1964).

7.3 "Burrell Manual for Gas Analysts," Seventh Edition (1951), Available from Burrell Corporation, 2223 Fifth Avenue, Pittsburgh, Pennsylvania 15219.

A3. Method 5—Determination of Particulate Emissions from Stationary Sources

1. Principle and Applicability

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and collected on glass fiber filter maintained at temperatures equal to or less than 120 ± 14°C (248 ± 25°F) or such other temperature as specified by an applicable subpart of the standards. The particulate mass is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards.

2. Apparatus

2.1 Sampling train. A schematic of the sampling train used in this method is shown in Figure 5-1.

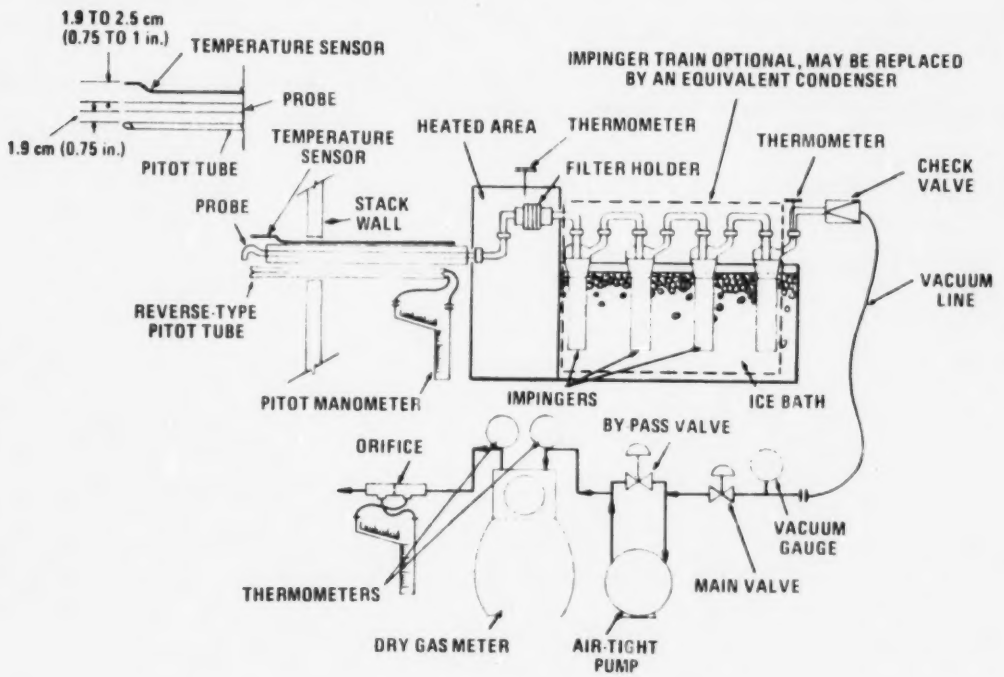


FIGURE 5-1. PARTICULATE-SAMPLING TRAIN.

Commercial models of this train are available. However, if one desires to build his own, complete construction details are described in APTD-0581; for changes from the APTD-0581 document and for allowable modifications to Figure 5-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576. Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein.

2.1.1 Probe nozzle–Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be $\leq 30^{\circ}$ and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall

be of the button-hook or elbow design, unless otherwise specified by the Administrator. The wall thickness of the nozzle shall be less than or equal to that of a 20 gauge tubing, i.e., 0.165 cm (0.065 in.) and the distance from the tip of the nozzle to the first bend or point of disturbance shall be at least two times the outside nozzle diameter. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used with approval from the Administrator.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 cm (1/8 in.) up to 1.27 cm (1/2 in.) (or larger if higher volume sampling trains are used) inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in the calibration section.

2.1.2 Probe liner—Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of no greater than 120 ± 14°C (248 ± 25°F) or no greater than such other temperature as specified by an applicable subpart of the standards. Since the actual temperature at the outlet of the probe is not monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 or calibrated according to the procedure outlined in APTD-0576 will be considered as acceptable.

Borosilicate or quartz glass probe liners shall be used for temperatures up to about 480°C (900°F) and quartz liners for temperatures up to about 900°C (1650°F). Both may be used at higher temperatures for short periods of time, but must be approved by the Administrator. The softening temperature for borosilicate is 820°C (1508°F) and for quartz it is 1500°C (2732°F).

When length limitations, i.e. greater than about 2.5 m (8.2 ft), are encountered at temperatures less than 320°C (608°F), stainless steel (316) or Incoloy 825[1] (both of seamless tubing), or other materials as approved by the Administrator, may be used. Metal probes for sampling gas streams at temperatures in excess of 320°C (608°F) must be approved by the Administrator.

2.1.3 Pitot tube—Type S, or other device approved by the Administrator, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other, not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3 cm (0.5 in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the largest sized nozzle shall be used to set the free space.

The pitot tube must also meet the criteria specified in Method 2 and calibrated according to the procedure in the calibration section of that method.

2.1.4 Differential pressure gauge—Inclined manometer capable of measuring velocity head to within 10% of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adaptable to field conditions and are not easy to use with pulsating flow. Thus, methods or other devices acceptable to the Administrator may be used when conditions warrant.

2.1.5 Filter holder—Borosilicate glass with a glass frit filter support and a silicone rubber gasket. Other materials of construction may be used with approval from the Administrator, e.g. if probe liner is stainless steel, then filter holder may be stainless steel. The holder design shall provide a positive seal against leakage from the outside or around the filter.

2.1.6 Filter heating system—Any heating system capable of maintaining a temperature around the filter holder during sampling of no greater than 120 ± 14°C (248 ± 25°F), or such other temperature as

[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

specified by an applicable subpart of the standards. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed such that temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than shown in APTD-0581 may be used.

2.1.7 Condenser–Any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law or (2) by passing the sample gas stream through a tared silica gel trap with exit gases kept below 20°C (68°F) and determining the weight gain.

Note: If "condensible particulate matter" is desired, in addition to moisture content, the following system shall be used–four impingers connected in series with ground glass, leak free fittings or any similarly leak free noncontaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (1/2 in.) ID glass tube extending to about 1.3 cm (1/2 in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

For purposes of writing the procedure of this method, the system described in the note above will be used for determining the moisture content of the stack gas. Modifications (e.g. using flexible connections between the impingers or using materials other than glass) may be used with approval from the Administrator.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices.

Unless otherwise specified by the Administrator, flexible vacuum lines may be used to connect the filter holder to the condenser.

2.1.8 Metering system–Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications in section 2 of this method are met. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

2.1.9 Barometer–Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which case the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

2.1.10 Gas density determination equipment–Temperature and pressure gauges and gas analyzer as described in Methods 2 and 3.

2.1.11 Temperature and pressure gauges–If Dalton's law is used, to monitor temperature and pressure at condenser outlet. The temperature gauge shall have an accuracy of 1°C (2°F). The pressure gauge shall be capable of measuring pressure to within 2.5 mm Hg (0.1 in. Hg). If silica gel is used in the condenser system the temperature and pressure must be measured before the silica gel component.

2.2 Sample recovery.

2.2.1 Probe liner and probe nozzle brushes–Nylon bristles with stainless steel wire handles. The probe brush shall have extensions, at least as long as the probe, of stainless steel, nylon, teflon, or similarly inert material. Both brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 Glass wash bottles–Two.

2.2.3 Glass sample storage containers–Chemically resistant, borosilicate narrow mouth glass bottles, for acetone washes, 500 ml or 1,000 ml. Screw cap closures shall be teflon rubber-backed liners or of such construction so as to be leak free and prevent chemical attack from the acetone. Other types of containers must be approved by the Administrator.

2.2.4 Petri dishes–For filter samples, glass or plastic, unless otherwise specified by the Administrator.

2.2.5 Graduated cylinder and/or balance–To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances are suitable for use here and in section 2.3.4.

2.2.6 Plastic storage containers–Air tight containers to store silica gel.

2.2.7 Funnel and rubber policeman–To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.3 Analysis.

2.3.1 Glass weighing dishes.

2.3.2 Desiccator.

2.3.3 Analytical balance–To measure to within 0.1 mg.

2.3.4 Balance–To measure to within 0.5 g.

2.3.5 Beakers–250 ml.

2.3.6 Hygrometer–To measure the relative humidity of the laboratory environment.

2.3.7 Temperature gauge–To measure the temperature of the laboratory environment.

3. Reagents

3.1 Sampling

3.1.1 Filters–Glass fiber filters, without organic binder exhibiting at least 99.95% efficiency (≤ 0.05% penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71. Test data from the supplier's quality control program is sufficient for this purpose.

3.1.2 Silica gel–Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received.

3.1.3 Water–When analysis of the material caught in the impingers is required, distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 Crushed ice.

3.1.5 Stopcock grease—Acetone insoluble, heat stable silicone grease. This is not necessary if screw-on connectors with teflon sleeves, or similar, are used.

3.2 Sample recovery.

3.2.1 Acetone—Reagent grade, ≤ 0.001% residue, in glass bottles. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers. Thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤ 0.001%) shall be used.

3.3 Analysis.

3.3.1 Acetone—Same as 3.2.1.

3.3.2 Desiccant—Anhydrous calcium sulfate, indicating type.

4. Procedure

4.1 Sampling. The sampling shall be conducted by competent personnel experienced with this test procedure.

4.1.1 Pretest preparation. All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified herein.

Weigh approximately 200-300 g of silica gel in air tight containers to the nearest 0.5 g. Record the total weight, both silica gel and container, on the container. More silica gel may be used but care should be taken during sampling that it is not entrained and carried out from the impinger. As an alternative, the silica gel may be weighed directly in the impinger or its sampling holder just prior to the train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label a filter of proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping container (glass or plastic petri dishes) and keep the filter in this container at all times except during sampling and weighing.

Desiccate the filters at 20 ± 5.6°C (68 ± 10°F) and ambient pressure for at least 24 hours and weigh at 6 or more hour intervals to a constant weight, i.e., ≤ 0.5 mg change from previous weighing, and record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50%.

4.1.2 Preliminary determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2 and moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate calculations. Estimates may be used. However, final results will be based on actual measurements made during the test.

Select a nozzle size based on the range of velocity heads such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the differential pressure gauge is capable of measuring the minimum velocity head value to within 10%, or as specified by the Administrator.

Select a suitable probe liner and probe length such that all traverse points can be sampled. Consider sampling from opposite sides for large stacks to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that the sampling time per point is not less than 2 min. or some greater time interval as specified by the Administrator and the sample volume that will be taken will exceed the required minimum total gas sample volume specified in the test procedures for the specific industry. The latter is based on an approximate average sampling rate. Note also that the minimum total sample volume is corrected to standard conditions.

It is recommended that 1/2 or an integral number of minutes be sampled at each point in order to avoid timekeeping errors.

In some circumstances, e.g. batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of collection train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and place approximately 200-300 g or more, if necessary, of preweighed silica gel in the fourth impinger. Record the weight of the silica gel and container to the nearest 0.5 g. Place the container in a clean place for later use in the sample recovery.

Using a tweezer or clean disposable surgical gloves, place the labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to not allow the sample gas stream to circumvent the filter. Check filter for tears after assembly is completed.

When glass liners are used, install selected nozzle using a Viton A O-ring when stack temperatures are less than 260°C (500°F) or an asbestos string gasket when temperatures are higher. The Viton A O-ring and asbestos string gasket are installed as a seal where the nozzle is connected to a glass liner. See APTD-0576 for details. When metal liners are used, install the nozzle as above or by a leak free direct mechanical connection. Mark probe with heat restraint tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Unless otherwise specified by the Administrator, attach a temperature probe to the metal sheath of the sampling probe so that the sensor extends beyond the probe tip and does not touch any metal. Its position should be about 1.9 to 2.54 cm (0.75 to 1 in.) from the pitot tube and probe nozzle to avoid interference with the gas flow.

Set up the train as in Figure 5-1, using, if necessary, a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. With approval from the Administrator, a glass cyclone may be used between the probe and filter holder.

Place crushed ice around the impingers.

4.1.4 Leak check procedure – After the sampling train has been assembled, turn on and set the filter and probe heating system to the power required to reach a temperature of 120 ± 14°C (248 ± 25°F) or such other temperature as specified by an applicable subpart of the standards for the leak check. (If water condensation is not a problem the probe and/or filter heating system need not be used.) Allow time for the temperature to stabilize. If a Viton A O-ring or other leak free connection is used in assembling the probe nozzle to the probe liner, leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum. (Note: A lower vacuum may be used provided that it is not exceeded during the test.) If an asbestos string is used, do not connect the probe to the train during the leak check. Instead, leak check the train as

above by first plugging the inlet to the filter holder. Then connect the probe to the train and leak check at about 25 mm Hg (1 in. Hg) vacuum. A leakage rate in excess of 4% of the average sampling rate of 0.00057 m^3/min. (0.02 cfm), whichever is less, is unacceptable in either case.

The following leak check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until 380 mm Hg (15 in. Hg) vacuum is reached. *Do not* reverse direction of by-pass valve. This will cause water to back up into the filter holder. If 380 mm Hg (15 in. Hg) is exceeded, either leak check at this higher vacuum or end the leak check as shown below and start over.

When the leak check is completed, first slowly remove the plug from the inlet to the probe or filter holder and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

Leak checks shall be conducted as described whenever the train is disengaged, e.g. for silica gel or filter changes during the test, prior to each test run, and at the completion of each test run. If leaks are found to be in excess of the acceptable rate, the test will be considered invalid. To reduce lost time due to leakage occurrences, it is recommended that leak checks be conducted between port changes.

4.1.5 Particulate train operation–During the sampling run, isokinetic sampling rate to within 10%, or as specified by the Administrator, of true isokinetic and the temperature around the filter of no greater than 120 ± 14°C (248 ± 25°F), , or as specified by an applicable subpart of the standards, shall be maintained.

For each run, record the data required on the example data sheet shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Take other data point readings at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer.

Clean the portholes prior to the test run to minimize chance of sampling the deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe are up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available for sampling trains using type S pitot tubes with 0.85 ± 0.02 coefficient and when sampling in air or a stack gas with equivalent density (molecular weight equal to 29 ± 4), which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. APTD-0576 details the procedure for using these nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomograph unless appropriate steps are taken to compensate for the deviations.

When the stack is under significant negative stack pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to avoid water backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes to minimize chance of extracting deposited material.

During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper temperature and add more ice and, if necessary, salt to maintain a temperature of less than

PLANT _____

LOCATION _____

OPERATOR _____

DATE _____

RUN NO _____

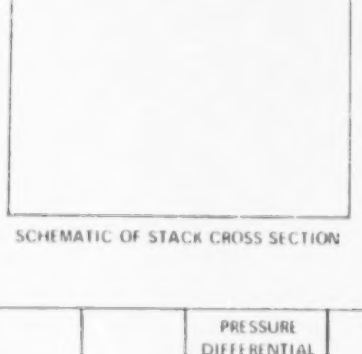
SAMPLE BOX NO _____

METER BOX NO _____

METER $\Delta H_@$ _____

C FACTOR _____

PITOT TUBE COEFFICIENT, C_p _____



SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE _____

BAROMETRIC PRESSURE _____

ASSUMED MOISTURE, % _____

PROBE LENGTH, m (ft) _____

NOZZLE IDENTIFICATION NO. _____

AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____

PROBE HEATER SETTING _____

LEAK RATE, m^3/min (cfm) _____

PROBE LINER MATERIAL _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE mm Hg (in Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S) mm(in.)H_2O	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		FILTER HOLDER TEMPERATURE, °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET °C (°F)	OUTLET °C (°F)		
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

FIGURE 5-2. PARTICULATE FIELD DATA.

20°C (68°F) at the condenser/silica gel outlet to avoid excessive moisture losses. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. After the new filter or filter assembly is installed conduct a leak check. The particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except for filter and silica gel changes. However, if approved by the Administrator, two or more trains may be used for a single test run when there are two or more ducts or sampling ports. The results shall be the total of all sampling train catches.

At the end of the sample run, turn off the pump, remove the probe and nozzle from the stack, and record the final dry gas meter reading. Perform a leak check at a vacuum equal to or greater than the maximum reached during sampling. Calculate percent isokinetic (see calculation section) to determine whether another test run should be made. If there is difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

4.2 Sample recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the fiber.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate, if present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground glass stoppers or plastic caps or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Place about 200 ml of this acetone in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Quantitatively remove any particulate matter and/or filter which adheres to the filter holder by carefully using a dry nylon bristle brush and/or a sharp-edged blade and place into this container. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the

probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash into a glass container in the following manner.

Distilled water may be used when approved by the Administrator or shall be used when specified by the Administrator. In these cases, save a water blank and follow Administrator's directions on analysis.

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse with acetone the inside parts of the Swagelok fitting in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting the probe and squirting acetone into its upper end, while rotating the probe so that all inside surfaces will be rinsed with acetone. Let the acetone drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe, hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone and quantitatively collect these washings in the sample container. After the brushing make a final acetone rinse of the probe as described above.

It is recommended that two people be used to clean the probe to minimize losing the sample. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints are wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter are collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label container to clearly identify its contents.

Container No. 3. Note color of indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to the original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure under analysis.

Impinger water. Treat the impingers or condenser as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ± 1 ml by using a graduated cylinder or, if available, to within ± 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

If analysis of the impinger catch is not required, discard the liquid after measuring and recording the volume or weight. If analysis of the impinger catch is required, leave the impingers intact to transfer the liquid, cap off the inlet, and pour the liquid through the outlet into the graduated cylinder or into a sample container after its weight has been determined.

If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

4.3 Analysis. Record the data required on the example sheet shown in Figure 5-3. Handle each sample container as follows:

Plant _____

Date _____

Run No. _____

Relative Humidity _____

Amount liquid lost during transport _____

Acetone blank volume, ml _____

Acetone wash volume, ml _____

Acetone blank concentration, mg/mg (equation 5-4) _____

Acetone wash blank, mg (equation 5-5) _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
		Less acetone blank	
		Weight of particulate matter	

	VOLUME OF LIQUID WATER COLLECTED		
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g	
FINAL			
INITIAL			
LIQUID COLLECTED			
TOTAL VOLUME COLLECTED		g*	ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml).

$$\frac{\text{INCREASE, g}}{1\ \text{g/ml}} = \text{VOLUME WATER, ml}$$

FIGURE 5-3. ANALYTICAL DATA.

Container No. 1. Leave in shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish and desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this section 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1% of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings and no more than 2 minutes exposure to the laboratory atmosphere (must be less than 50% relative humidity) during weighing.

Container No. 2. Note level of liquid in container and confirm on analysis sheet whether or not leakage occurred during transport. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel to the nearest 0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250 ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

5. Calibration

Maintain a laboratory log of all calibrations.

5.1 Probe nozzle. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make 3 separate measurements using different diameters each time and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use.

Each nozzle shall be permanently and uniquely identified.

5.2 Pitot tube. The pitot tube shall be calibrated according to the procedure outlined in Method 2.

5.3 Dry gas meter and orifice meter. Both meters shall be calibrated according to the procedure outlined in APTD-0576. When diaphragm pumps with by-pass valves are used, check for proper metering system design by calibrating the dry gas meter at an additional flow rate of 0.0057 m^3/min. (0.2 cfm) with the by-pass valve fully opened and then with it fully closed. If there is more than ± 2% difference in flow rates when compared to the fully closed position of the by-pass valve, the system is not designed properly and must be corrected.

5.4 Probe heater calibration. The probe heating system shall be calibrated according to the procedure contained in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

5.5 Temperature gauges. Calibrate dial and liquid filled bulb thermometers against mercury-in-glass thermometers. New thermocouples need not be calibrated. Calibrate used thermocouples against new ones. For other devices, check with the Administrator.

6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

6.1 Nomenclature

A_n = Cross sectional area of nozzle, m^2 (ft^2)

B_{ws} = Water vapor in the gas stream, proportion by volume

C_a = Acetone blank residue concentration, mg/mg

c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf)

I = Percent of isokinetic sampling

m_n = Total amount of particulate matter collected, mg.

M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)

m_a = Mass of residue of acetone after evaporation, mg

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg)

P_s = Absolute stack gas pressure, mm Hg (in. Hg)

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.83 in. Hg-ft^3/°R-lb-mole)

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °K (°R)

T_s = Absolute average stack gas temperature (see Figure 5-2), °K (°R)

T_{std} = Standard absolute temperature, 293°K (528°R)

V_a = Volume of acetone blank, ml

V_{aw} = Volume of acetone used in wash, ml

V_{lc} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3, ml).

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf)

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by Method 2, Equation 2-7 using data obtained from Method 5, m/sec (ft/sec)

W_a = Weight of residue in acetone wash, mg

ΔH = Average pressure differential across the orifice (see Figure 5-2), meter, mm H_2O (in. H_2O)

ρ_a = Density of acetone, mg/ml (see label on bottle)

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml)

θ = Total sampling time, min.

13.6 = Specific gravity of mercury

60 = sec/min

100 = Conversion to percent

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.3 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in. Hg) by using Equation 5-1.

$$V_{m(std)} = V_m\left(\frac{T_{std}}{T_m}\right)\left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}\right] = K\ V_m\left[\frac{P_{bar} + \Delta H/13.6}{T_m}\right] \qquad \text{Equation 5-1}$$

where:

K = 0.3855 °K/mm Hg for metric units

= 17.65 °R/in. Hg for English units

6.4 Volume of water vapor.

$$V_{w(std)} = V_{lc}\left(\frac{\rho_w}{M_w}\right)\left(\frac{RT_{std}}{P_{std}}\right) = K\ V_{lc} \qquad \text{Equation 5-2}$$

where

K = 0.00134 m^3/ml for metric units

= 0.0472 ft^3/ml for English units

6.5 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \text{Equation 5-3}$$

6.6 Acetone blank concentration.

$$C_a = \frac{m_a}{V_a\,\rho_a} \qquad \text{Equation 5-4}$$

6.7 Acetone wash blank.

$$W_a = C_a\,V_{aw}\,\rho_a \qquad \text{Equation 5-5}$$

6.8 Total particulate weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3).

6.9 Particulate concentration.

$$c_s = (0.001\ g/mg)\,(m_n/V_{m(std)}) \qquad \text{Equation 5-6}$$

6.10 Conversion factors:

From	To	Multiply by
scf	m^3	0.0283
g/ft^3	gr/ft^3	15.4
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.34

6.11 Isokinetic variation.

6.11.1 Calculations from raw data.

$$I = \frac{100\, T_s \left[K\, V_{lc} + (V_m/T_m)(P_{bar} + \Delta H/13.6)\right]}{60\, \theta\, v_s\, P_s\, A_n} \qquad \text{Equation 5-7}$$

where:

K = 0.00346 mm Hg-m^3/ml-°K for metric units

= 0.00267 in. Hg-ft^3/ml-°R for English units

6.11.2 Calculations from intermediate values.

$$I = \frac{T_s\, V_{m(std)}\, P_{std}\, 100}{T_{std}\, v_s\, \theta\, A_n\, P_s\, 60\,(1\text{-}B_{ws})}$$

$$= K\, \frac{T_s\, V_{m(std)}}{P_s\, v_s\, A_n\, \theta\,(1\text{-}B_{ws})} \qquad \text{Equation 5-8}$$

where:

K = 4.323 for metric units

= 0.0944 for English units

6.12 Acceptable results. If $90\% \leq I \leq 110\%$, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may option to accept the results. Use reference 7.4 to make judgments. Otherwise, reject the results and repeat the test.

7. References

7.1 Addendum to Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, Dec. 6, 1967.

7.2 Martin, Robert M., Construction Details of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0581.

7.3 Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, Environmental Protection Agency, APTD-0576.

7.4 Smith, W.S., R. T. Shigehara, and W. F. Todd, A Method of Interpreting Stack Sampling Data, Paper presented at the 63rd Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14-19, 1970.

7.5 Smith, W. S., et al., Stack Gas Sampling Improved and Simplified with New Equipment, APCA paper No. 67-119, 1967.

7.6 Specifications for Incinerator Testing at Federal Facilities, PHS, NCAPC, 1967.

APPENDIX B. STATISTICAL METHODS

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B.1 Statistical Model for Particulate Concentration Data

The preliminary test plan for the collaborative test included a detailed discussion of the plan for the statistical analysis of the data in order to insure that the components of interest could be validly estimated. The sampling plan called for 5 runs each week with 4 paired trains per run. One laboratory team (console operator and two technicians) would operate a paired train alone, while 6 laboratories would independently operate a single train of the paired train system. To insure that the results of the paired-train laboratory were indicative of the results one could expect of other laboratories, three independent teams were used as the paired-train laboratory, one for each week of the test. The remaining laboratories were to be paired, and the pairings would remain constant during the course of the test.

The analytical method to be used was an analysis of variance according to the model

$$Y_{ij} = \mu + \rho_i + \gamma_j + \epsilon_{ij}$$

where

Y_{ij} – determined concentration from laboratory j in run i

μ – overall mean

ρ_i – effect due to run i

γ_j – effect due to lab j

and

ϵ_{ij} – random error associated with Y_{ij}.

Laboratories and runs are assumed to be random effects. The model is an additive or no-interaction model. The term for the interaction between runs and laboratories is then used as the error term in the ANOVA.

The data are investigated in two forms. First the results of each week's runs are submitted to the ANOVA procedure. There are 8 trains for each of these analyses, and a proposed 5 runs, for a total of 40 concentration determinations in each week. The single-week data are principally the source of the within-laboratory or sampling error term. There are two potential sources for this term.

The usual estimate of sampling error comes from the run by train interaction term. In addition, a preliminary test of the paired particulate sampling train using a single laboratory team demonstrated that the two concentrations thus obtained could be considered replicates. An error variance of

$$s^2 = \sum_{i=1}^{k} \sum_{j=1}^{2} (Y_{ij} - \overline{Y}_{i\cdot})^2$$

where

$\overline{Y}_{i\cdot} = 1/2(Y_{i1} + Y_{i2})$

k – number of runs

can be calculated if the paired-train laboratory can be shown to be obtaining replicate samples. This estimate has k df associated with it, one from each sampling run.

If the laboratory term is significant, the laboratory SS can be partitioned into SS for various hypotheses of interest. This is done by the use of orthogonal contrasts among the means, as described in Snedecor and Cochran.[14] A contrast is of the form

$$\sum_{i=1}^{n} C_i \bar{X}_i$$

where

$\bar{X}_i$ – i^{th} sample mean

C_i —constant

and

$\sum_{i=1}^{n} C_i = 0.$

Two contrasts, $\sum_{i=1}^{n} C_i \bar{X}_i$ and $\sum_{i=1}^{n} d_i \bar{X}_i$, are said to be orthogonal if

$$\sum_{i=1}^{n} C_i di = 0.$$

If the contrasts are chosen to be orthogonal, then they can be used to partition the SS for a particular term. The hypothesis to be tested by a contrast is

$$H_o: \sum C_i \bar{X}_i = 0,$$

and the SS due to the hypothesis are calculated as

$$SS_{H_o} = \frac{(\sum C_i \bar{X}_i)^2}{\sum C_i^2}$$

with 1 df for each contrast.

For this study, contrasts are included which satisfy the questions of interest. If the values for the paired-train laboratory are to be used as replicates, then it must be shown that they are estimating the same mean level. The differences between the paired laboratories on a single train are to be used to estimate the laboratory bias variance, and a contrast is used for each of these pairs. The differences among pairs are also investigated, so that a contrast for this term is included. The contrasts used for each analysis are summarized in Table B1.

TABLE B1. CONTRASTS AMONG LABORATORY MEANS

Contrasts	Laboratory Mean							
	101A	101B	104	105	106	107	108	109
Week 1								
1	1	−1	0	0	0	0	0	0
2	1	1	1	1	−1	−1	−1	−1

Contrasts	Laboratory Mean					
	104	105	106	107	108	109
3 Week						
1	1	−1	0	0	0	0
2	0	0	1	−1	0	0
3	0	0	0	0	1	−1
4	2	2	−1	−1	−1	−1

For the single week's analysis, the first contrast tests for the equality of means between the two results from the paired-laboratory train. The second is an investigation of any differences among pairs of laboratories. The contrasts are shown in Table B1 for week 1, and are identical for the second and third week, with the substitution of the other laboratories running the paired-laboratory train. For the three week analysis, contrasts 1, 2 and 3 are tests for equality between paired laboratories, while the fourth is another test for differences among pairs.

Along with the contrasts among the means, the error SS can be partitioned in a similar manner to provide a separate error term for each contrast. This is done to insure that a proper divisor is used in the F-tests, for the case where the error variance may not be homogeneous for all terms. The error term for each contrast is obtained by applying the contrasts separately to each run, then obtaining a sums of squares from these run contrasts. These subdivisions of the error term each have $(r - 1)$ df associated with them, where r is the number of runs.

The results of these analyses are summarized in ANOVA tables, from which variance components are estimated and significance is determined for the factors of interest. These are shown in subsequent appendices for both the particulate concentration from Method 5, and the corrected concentration, as pertains to incinerators.

B.2 Precision Estimation and Tests of Hypotheses for Method 5

The particulate concentrations shown in Table 1 are submitted to statistical analyses according to the model in Appendix B.1. The three weeks of results are analyzed separately first, using the concentration from all 8 trains. The ANOVA tables generated from these analyses are shown in Table B2.

TABLE B2. ANOVA FOR METHOD 5 CONCENTRATION DETERMINATIONS, INDIVIDUAL WEEKS

Week	Source	df	SS	MS	F	EMS
1	Runs	2	4,610.25	2,305.13	11.25*	
Mean = 121.83	Labs	7	4,068.19	581.17	2.84*	$\sigma^2 + 3\sigma^2_L$
	1 vs 2	1	123.40	123.40	14.98†	
	(1-4) vs (5-8)	1	593.79	593.79	<1†	
	Error	14	2,867.98	204.86		σ^2
		2	16.47	8.24		
		2	1,530.85	715.43		
	Total	23	11,546.42			
2	Runs	4	15,511.33	3,877.83	24.57*	
Mean = 123.19	Labs	7	2,193.13	313.30	1.98†	$\sigma^2 + 5\sigma^2_L$
	Error	28	4,419.17	157.85		σ^2
	Total	39	22,123.63			
3	Runs	4	26,964.76	6,741.19	19.71*	
Mean = 148.64	Labs	7	6,398.31	914.04	2.67*	$\sigma^2 + 5\sigma^2_L$
	1 vs 2	1	414.74	414.74	2.42†	
	(1-4) vs (5-8)	1	2,373.14	2,373.14	2.23†	
	Error	27	9,236.55	342.08		σ^2
		4	684.45	171.11		
		4	4,259.95	1,064.99		
	Total	38	42,599.62			

*Significant at 5% level.
†Not significant.

The labs term is significant for the 1st and 3rd weeks of the test. From each of these, contrasts are made between the means of the paired-laboratory trains. Using the error term associated with this contrast, an F-ratio is calculated to test for the equality of the two means. In both cases, the calculated F's are less than the tabled F-values, and the hypotheses are accepted. This implies that the trains are obtaining replicates, and an estimated sampling error term can be estimated from within the replicates. This is done according to the formula in Appendix B.1 for Labs 101 and 103, and also for Lab 102, where no significant difference existed among the 8 trains. These estimates are tested for equality using Bartlett's test,[14] which gives a significance level of 0.03. Pooling the estimates, then gives $s_p^2 = 190.81$, with 13 df.

In each week's data, the error term has an EMS of σ^2, the within-laboratory variance. Testing these by Bartlett's test gives a significance level of 0.13, so the hypothesis of equality is accepted. These may also be pooled, then, to give

$$\sigma_p^2 = 239.48$$

with 69 df. The estimated standard deviations for the two cases are 13.81 and 15.48, respectively, which indicates that either could serve as a valid estimate of σ^2.

The second hypothesis tested is one dealing with the pairs of trains. The four paired trains are split into two groups, and if a difference among pairs exists, it should be reflected in this contrast. However, in both the first and the third week's data, there was no detectable difference among the pairs.

In Table B3, the ANOVA for the 6 laboratories through 13 runs is summarized. This analysis is used to estimate the laboratory bias term for the method. The laboratory term for the analysis is shown to be significant, which indicates that not all trains have the same true mean. Contrasts among the laboratory means are then used to determine significance and estimate the variance components.

TABLE B3. ANOVA FOR METHOD 5 CONCENTRATION DETERMINATIONS, 3-WEEK ANALYSIS

Source	df	SS	MS	F	EMS
Runs	12	36,593.44	3,049.55	16.40*	–
Labs	5	4,436.18	887.24	4.77*	$\sigma^2 + 13\,\sigma_L^2$
4 vs 5	1	2,117.72	2,117.72	42.30*	
6 vs 7	1	184.66	184.66	271.56*	
8 vs 9	1	858.13	858.13	30.12*	
(4,5) vs (6,7) vs (8,9)	1	1,175.46	1,175.46	4.57*	
Error	59	11,158.60	189.13		σ^2
4 vs 5	12	600.86	50.07		
6 vs 7	12	8.20	0.68		
8 vs 9	12	341.86	28.49		
(4,5) vs (6,7) vs (8,9)	12	3,087.34	257.28		
Total	76	52,188.22			

*Significant at 5% level.

The three contrasts related to the laboratory bias term are those comparing laboratories operating on the same paired train. In each case, F-ratios calculated using the error terms calculated for the contrast show that significant differences do exist. These SS are then pooled to give laboratory bias SS of $SS_L = 3160.51$, with 3 df. The laboratory bias MS, then, is $MS_L = 1053.50$, and has expected value of $\sigma^2 + 13\,\sigma_L^2$. Substituting the estimated sampling error term gives

$$\hat{\sigma}_L^2 = \frac{MS_L - \hat{s}_p^2}{13}$$

$$= \frac{1053.50 - 190.81}{13}$$

$$= 66.36,$$

with 3 df.

The pairs term is significant in this analysis, but the SS due to pairs is 1175.46, which is close to the SS for labs. The indication is that this is simply another estimate of the laboratory bias component. In addition, if spatial/temporal changes in the gas flow are the cause of the differences, the error term for the contrast should be large, but this is not the case. The error MS for pairs is 257.28. Using an F-ratio to test for equality, a test statistic of $F_c = 1.35$ is calculated. The critical value from a table of the F-distribution with 12 and 13 df is $F(12, 13) = 1.47$, using a significance level of 25%. Since F_c does not exceed 1.47, no difference can be shown even at that level.

B.3 Rank Test for Equality of Laboratories

In order to test whether the separate laboratories obtain equivalent results, the concentrations are submitted to analysis using a nonparametric analysis of variance technique. The purpose of this test is to determine whether there is an ordering of laboratories independent of concentration and, if so, to what it can be attributed.

The test chosen is the Friedman test, a two-way procedure which allows for a blocking factor, in this case runs. The data are ranked across runs, and then summed for each laboratory. These rank sums, R_{ij}, form the basis for the test. If all laboratories are equivalent, the R_{ij} should be approximately equal. The test statistic is

$$\chi_r^2 = \frac{12}{Nk(k+1)} \sum_{j=1}^{k} R_{ij}^2 - 3N(k+1)$$

where

R_{ij} – rank sum for laboratory j

N – number of runs

k – number of labs.

This value is then compared to a table of the chi-square distribution with $k - 1$ df to determine significance.

The test is applied separately to each week's data, using the six results from the labs running a single train, plus the average of the two results from the dual train. The value of χ_r^2 along with its df and significance level is shown in Table B4 for these data. In addition, the test is applied to the data from the six laboratories that completed all 13 runs, and these results included in the table.

TABLE B4. SUMMARY OF FRIEDMAN TEST

Test	χ_r^2	df	Significance Level
Week 1	7.71	6	0.26
Week 2	11.21	6	0.08
Week 3	13.82	6	0.03
6 Labs	21.04	5	0.001

The results from the separate weeks are inconclusive, with one insignificant, one marginally significant and one significant result. The 6-laboratory test, however, shows that the ordering is significant at a level of 0.001, showing a strong tendency for the labs to be ordered relative to one another, irrespective of position or pairing. The rank sums which are most nearly equal are the pairs Lab 107 and Lab 109, and Lab 106 and Lab 108, which do not represent the pairing of the laboratories with respect to the trains. The apparent conclusion, then, is that this phenomenon is unrelated to the stack flow, but rather reflects differences in such things as sample recovery techniques and equipment operation.

B.4 Weighted Coefficient of Variation Estimates

The technique used for obtaining estimates of the coefficients of variation of interest is to use a linear combination of the individual beta values obtained. The linear combination used will be of the form

$$\hat{\beta} = \frac{1}{k} \sum_{j=1}^{k} \beta_j$$

or

$$\hat{\beta} = \frac{1}{k} \sum_{j=1}^{k} \omega_j \hat{\beta}_j$$

where $\hat{\beta}_j$ is the j^{th} coefficient of variation estimate, k is the total number of estimates, and ω_j is a weight applied to the j^{th} estimate. The weighted values are used if the coefficient of variation estimates are based on unequal sample sizes.

As previously discussed, the individual estimate of β is obtained as

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}}$$

for a sample of size n. The factor α_n is defined as[11]

$$\alpha_n = \sqrt{\frac{2}{3}} \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n-1}{2}\right)}$$

where Γ represents the standard gamma function. Thus for k equal-size samples, the best estimator is simply the arithmetic mean of the individual beta values.[11]. However, if the sample sizes are unequal, weighting is more desirable in that it provides for more contribution from those values derived from larger samples. There is more variability in the beta values obtained from the smaller samples, as can be seen by inspecting the variance of the estimator. We have that

$$\begin{aligned} \text{Var}(\hat{\beta}) &= \text{Var}\left(\frac{\alpha_n s}{\bar{x}}\right) \\ &= \alpha_n^2 \, \text{Var}\left(\frac{s}{\bar{x}}\right) \\ &= \alpha_n^2 \left[\frac{\beta^2}{2n}(1 + 2\beta^2)\right] \end{aligned}$$

for normally distributed samples,[1] and true coefficient of variation, β. Rewriting this expression, we have

$$\text{Var}(\hat{\beta}) = \frac{\alpha_n^2}{n}\left[\frac{\beta^2}{2}(1 + 2\beta^2)\right]$$

and all terms are constant except for α_n^2 and n. Thus, the magnitude of the variance changes with respect to the factor α_n^2/n. Now, since α_n decreases as n increases, the factor α_n^2/n must decrease as n increases, and the variance is reduced.

The weights, ω_j, are determined according to the technique used in weighted least squares analysis[8], which gives a minimum variance estimate of the parameter. The individual weight, ω_i, is computed as the inverse of the variance of the estimate, $\hat{\beta}_i$, and then standardized. Weights are said to be standardized when

$$\frac{1}{k} \sum_{j=1}^{k} \omega_j = 1$$

To standardize, the weights are divided by the average of the inverse variances for all the estimates. Thus, we can write

$$\omega_i = \frac{u_i}{\bar{u}}$$

where

$$u_i = \frac{1}{\text{Var}(\hat{\beta}_i)}$$

and

$$\bar{u} = \frac{1}{k} \sum_{j=1}^{k} \frac{1}{\text{Var}(\hat{\beta}_j)}$$

Now, from the above expressions we can determine u_i, $\bar{u}$ and ω_i for the beta estimates. For any estimate, $\hat{\beta}_i$,

$$u_i = \frac{1}{\text{Var}(\hat{\beta}_i)}$$

$$= \frac{n_i}{\alpha_{n_i}^2} \left[\frac{2}{\beta^2 (1 + 2\beta^2)} \right]$$

for sample size n_i, and

$$\bar{u} = \frac{1}{k} \sum_{j=1}^{k} \frac{1}{\text{Var}(\hat{\beta}_j)}$$

$$= \frac{1}{k} \sum_{j=1}^{k} \frac{n_j}{\alpha_{n_j}^2} \left[\frac{2}{\beta^2 (1 + 2\beta^2)} \right]$$

$$= \frac{1}{k} \left[\frac{2}{\beta^2 (1 + 2\beta^2)} \right] \sum_{j=1}^{k} \frac{n_j}{\alpha_{n_j}^2}$$

Thus, the nth weight, ω_i, is

$$\omega_i = \frac{u_i}{\bar{u}}$$

$$= \frac{\dfrac{n_i}{\alpha_{n_i}^2}\left[\dfrac{2}{\beta^2\,(1+2\beta^2)}\right]}{\dfrac{1}{k}\left[\dfrac{2}{\beta^2\,(1+2\beta^2)}\right]\sum_{j=1}^{k}\dfrac{n_j}{\alpha_{n_j}^2}}$$

$$= \frac{\dfrac{n_i}{\alpha_{n_i}^2}}{\dfrac{1}{k}\sum_{j=1}^{k}\dfrac{n_j}{\alpha_{n_j}^2}}$$

$$= \frac{\dfrac{kn_i}{\alpha_{n_i}^2}}{\sum_{j=1}^{k}\dfrac{n_j}{\alpha_{n_j}^2}}$$

The estimated coefficient of variation is

$$\hat{\beta} = \frac{1}{k}\sum_{j=1}^{k}\omega_j\hat{\beta}_j$$

$$= \frac{1}{k}\sum_{i=1}^{k}\frac{kn_i\alpha_{n_i}^2}{\sum_{j=1}^{k}\dfrac{n_j}{\alpha_{n_j}^2}}\,\hat{\beta}_i$$

$$\hat{\beta}_c = \left[\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}\right]^{-1}\sum_{i=1}^{k}\frac{n_i}{\alpha_{n_i}^2}\,\frac{\alpha_{n_i}s}{\bar{x}}$$

$$= \left[\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}\right]^{-1}\sum_{i=1}^{k}\frac{n_i s}{\alpha_{n_i}\bar{x}}$$

B.5 Precision Estimation for Velocity Determination

In a previous report, it was shown that the precision of the determination of velocity varies according to the actual velocity, and that a valid model is of the form,

$$\sigma = \beta\ \mu$$

and

$$\sigma_b = \beta_b\mu$$

for the within- and between-laboratory components, respectively. Thus, to provide estimates of the standard deviations of interest, the coefficients of variation, β and β_b, are estimated and the standard deviations expressed as percentages of an unknown mean value.

The technique for obtaining estimated coefficients of variation is discussed in Appendix B.4. The between-laboratory coefficient of variation, β_b, is estimated as

$$\hat{\beta}_b = \frac{1}{13} \sum_{i=1}^{13} \alpha_n \frac{s_i}{\bar{x}_i}$$

where

$\bar{x}_i$ – the sample mean of the i^{th} run, across laboratories

s_i – sample standard deviation of the i^{th} run

and

α_n – finite correction factor used to correct for the bias in s.

Since all the estimates are based upon 6 determinations, no weighting procedure is used, and $\alpha_{n_i} = \alpha_n = 1.0509$. The means and standard deviations for the runs are shown in Table B5. These values are substituted into the above equation to obtain

TABLE B5. RUN DATA SUMMARY
(m/sec)

Run	Mean	Standard Deviation	Coefficient of Variation
1	14.39	0.52	0.0534
2	15.06	0.80	0.0375
7	14.62	0.55	0.0358
8	14.65	0.46	0.0340
9	14.80	0.50	0.0316
3	15.45	0.73	0.0473
4	15.64	0.53	0.0561
5	15.53	0.87	0.0491
6	14.94	0.73	0.0387
10	15.19	0.59	0.0382
11	15.26	0.58	0.0456
12	15.58	0.63	0.0340
13	15.39	0.70	0.0408

$$\hat{\beta} = 0.043.$$

There are 5 df associated with this estimate from the 6 laboratories. The estimated between-laboratory standard deviation, then, is

$$\hat{\sigma}_b = \hat{\beta}_b \mu$$

$$= (0.043)\,\mu$$

or 4.3% of the mean velocity.

The within-laboratory coefficient of variation, β, is estimated from the values obtained from each collaborator in a given block. There are 12 of these collaborator-block combinations, which gives

$$\hat{\beta} = \frac{1}{12} \sum_{j=1}^{12} \omega_j \frac{s_j}{\bar{x}_j}$$

where

s_j – standard deviation for collaborator-block j

$\bar{x}_j$ – mean of collaborator-block j results

and

ω_j – weight applied to the j^{th} estimate.

The weighting procedure is used since the two blocks are of unequal size, and is discussed in Appendix B.4. The weights incorporate the finite correction factor for the bias in s, and give more weight to the values obtained from the larger blocks.

The means and standard deviations are shown in Table B6, for the 12 collaborator-block combinations.

TABLE B6. COLLABORATOR-BLOCK DATA SUMMARY
(m/sec)

Collaborator	Mean	Standard Deviation	Coefficient of Variation
Block 1			
Lab 104	13.97	0.28	2.02
Lab 105	14.30	0.17	1.22
Lab 106	14.79	0.27	1.83
Lab 107	14.92	0.29	1.91
Lab 108	15.55	0.48	3.07
Lab 109	14.70	0.37	2.53
Block 2			
Lab 104	14.47	0.28	1.93
Lab 105	14.88	0.37	2.46
Lab 106	15.60	0.29	1.87
Lab 107	15.74	0.34	2.19
Lab 108	16.26	0.24	1.48
Lab 109	15.28	0.40	2.62

Substituting into the above equation gives an estimated coefficient of variation of

$$\hat{\beta} = 0.022$$

with 60 df. The within-laboratory standard deviation is estimated as

$$\hat{\sigma} = \hat{\beta}\,\mu$$

$$= (0.022)\,\mu$$

or 2.2% of the mean value.

The laboratory bias coefficient of variation is estimated from the above as

$$\hat{\beta}_L = \sqrt{\beta_b^2 - \beta^2}$$

$$= \sqrt{(0.043)^2 - (0.022)^2}$$

$$= 0.037.$$

The laboratory bias standard deviation, then, is

$$\hat{\sigma} = \hat{\beta}_L\,\mu$$

$$= (0.037)\mu$$

or 3.7% of the mean value. There are 5 df associated with this estimate from the between-laboratory term.

B.6 Precision Estimation for Method 3

a. Model

The Orsat data and dry gas molecular weight from the 9 laboratories that participated in the test are submitted to an ANOVA each according to the same model. The three weeks are treated separately according to the model

$$Y_{ij} = \gamma_i + \epsilon_{ij}$$

where

Y_{ij} – determination by collaborator i in run j

γ_i – effect due to laboratory i

and

ϵ_{ij} – random error associated with Y_{ij}.

All effects are assumed to be random. The first week there were 3 runs by 6 laboratories and in the next two weeks there were 5 runs by 7 laboratories. In the second week, one laboratory did not make a determination, and a value was substituted according to the formula given in Snedecor and Cochran.[14] This is compensated for by reducing by 1 the degrees of freedom for error. The model assumes runs to be replicate determinations, since a preliminary test showed the runs factor insignificant in all cases.

b. CO_2

The determinations of the CO_2 level made by the collaborators are shown in Table 9 in the body of the report. Performing the analysis of variance according to the model in a. above, three ANOVA tables are generated, and these are shown in Table B7.

TABLE B7. ANOVA FOR CO_2 DETERMINATION

Source	df	SS	MS	F	EMS
Week 1					
Labs	5	0.97	0.19	1.58†	$\sigma^2 + 3\sigma^2_L$
Error	12	1.45	0.12		σ^2
Total	17	2.43			
Week 2					
Labs	6	4.21	0.70	35.00*	$\sigma^2 + 5\sigma^2_L$
Error	27	0.65	0.02		σ^2
Total	33	4.86			
Week 3					
Labs	6	2.96	0.49	9.80*	$\sigma^2 + 5\sigma^2_L$
Error	28	1.41	0.05		
Total	34	4.37			

†Not significant.
*Significant at 5% level.

The error mean square has an expected value (EMS) of σ^2, the true within-laboratory variance. The estimated within-laboratory variance, then, is obtained by pooling the sums of squares and df for error into a single estimate. The estimated within-laboratory variance is

$$\hat{\sigma}^2 = \frac{SS_{\text{pooled}}}{df_{\text{pooled}}}$$

$$= \frac{[1.45 + 0.65 + 1.41]}{12 + 27 + 28}$$

$$= \frac{2.51}{67}$$

$$= 0.04$$

with 67 df. The within-laboratory standard deviation is estimated to be $\hat{\sigma} = \sqrt{\hat{\sigma}^2}$

= 0.20 percent CO_2 by volume

The laboratory term is significant for weeks 2 and 3. For each, the expected value of the mean square for laboratories is $\sigma^2 + 5\sigma^2_L$, which gives an estimated value of

$$\hat{\sigma}^2_L = \frac{MS_L - \hat{\sigma}^2}{5}$$

for each week of the test, where MS_L is the mean square for laboratories. The two estimates are

$$\hat{\sigma}^2_{L_2} = \frac{0.70 - 0.02}{5}$$

$$= \frac{0.68}{5}$$

$$= 0.14$$

and

$$\hat{\sigma}^2_{L_3} = \frac{0.49 - 0.05}{5}$$

$$= \frac{0.44}{5}$$

$$= 0.09,$$

each with 6 df from the 7 laboratories. The combined estimate is taken to be the average of the two values, since each is based on the same number of df. This gives

$$\hat{\sigma}^2_L = \frac{1}{2}\left(\hat{\sigma}^2_{L_2} + \sigma^2_{L_3}\right)$$

$$= \frac{1}{2}(0.14 + 0.09)$$

$$= 0.12$$

with 6 df. The estimated laboratory bias standard deviation is

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}^2_L}$$

$$= \sqrt{0.12}$$

$$= 0.35 \text{ percent of } CO_2.$$

The between-laboratory variance is estimated from the above to be

$$\hat{\sigma}^2_b = \hat{\sigma}^2 + \hat{\sigma}^2_L$$

$$= 0.04 + 0.12$$

$$= 0.16.$$

This gives an estimated between-laboratory standard deviation of

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}^2_b}$$

$$= \sqrt{0.16}$$

$$= 0.40 \text{ percent } CO_2.$$

There are 6 df associated with this estimate, due to the laboratory bias term.

c. O_2

The oxygen determinations from Table 10 are submitted to the ANOVA procedure outlined in section a. above. The resultant tables are shown in Table B8.

TABLE B8. ANOVA FOR O_2 DETERMINATION

Source	df	SS	MS	F	EMS
Week 1					
Labs	5	3.19	0.64	5.33*	$\sigma^2 + 3\sigma^2_L$
Error	12	1.45	0.12		σ^2
Total	17	4.64			
Week 2					
Labs	6	8.52	1.42	23.67*	$\sigma^2 + 5\sigma^2_L$
Error	27	1.43	0.06		σ^2
Total	33	9.95			
Week 3					
Labs	6	12.12	2.02	15.54*	$\sigma^2 + 5\sigma^2_L$
Error	28	3.53	0.13		σ^2
Total	34	15.65			
*Significant at 5% level.					

The expected mean square of the error term is σ^2, the within-laboratory variance. Pooling the three estimates obtained gives,

$$\hat{\sigma}^2 = \frac{SS_{\text{pooled}}}{df_{\text{pooled}}}$$

$$= \frac{[1.45 + 1.43 + 3.53]}{12 + 27 + 28}$$

$$= 6.41/67$$

$$= 0.10$$

with 67 df. This gives an estimated within-laboratory standard deviation of

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= \sqrt{0.10}$$

$$= 0.32.$$

The laboratory term in the ANOVA is significant in all three sets of data. The EMS of the lab term is $\sigma^2 + k\sigma^2_L$, where $k = 3, 5, 5$, respectively, for the three weeks. The three estimates obtained are

$$\hat{\sigma}^2_{L_1} = 0.14$$

$$\hat{\sigma}^2_{L_2} = 0.27$$

and

$$\hat{\sigma}^2_{L_3} = 0.38$$

with 5, 6, and 6 df, respectively. Pooling these estimates gives

$$\hat{\sigma}^2_L = \frac{5(0.14) + 6(0.27) + 6(0.38)}{17}$$

$$= 0.27.$$

There are 6 df associated with this estimate. The estimated laboratory bias standard deviation, then is

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}^2_L}$$

$$= \sqrt{0.27}$$

$$= 0.52.$$

Combining the above estimates gives an estimated between-laboratory variance of

$$\hat{\sigma}_b^2 = \hat{\sigma}^2 + \hat{\sigma}_L^2$$

$$= 0.10 + 0.27$$

$$= 0.37$$

with 6 df. The between-laboratory standard deviation is estimated as

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}_b^2}$$

$$= \sqrt{0.37}$$

$$= 0.61 \text{ percent } O_2 .$$

d. Md

The dry gas molecular weights calculated by the collaborators are shown in Table 11 for the three weeks of the test. Using the model in section a. above, the ANOVA tables are generated and the ANOVA are shown in Table B9.

TABLE B9. ANOVA FOR Md DETERMINATION

Source	df	SS	MS	F	EMS
Week 1					
Labs	5	0.0150	0.0030	1.25†	$\sigma^2 + 3\sigma_L^2$
Error	12	0.0291	0.0024		σ^2
Total	17	0.0441			
Week 2					
Labs	6	0.0493	0.0082	16.40*	$\sigma^2 + 5\sigma_L^2$
Error	27	0.0136	0.0005		σ^2
Total	33	0.0629			
Week 3					
Labs	6	0.0209	0.0035	5.00*	$\sigma^2 + 5\sigma_L^2$
Error	28	0.0189	0.0007		σ^2
Total	34	0.0398			

†Insignificant.
*Significant at 5% level.

The EMS of the error term is σ^2, the within-laboratory variance. The mean squares for error from the three weeks are combined into a single estimate by pooling the sums of squares and df. The result is

$$\hat{\sigma}^2 = \frac{SS_{\text{pooled}}}{df_{\text{pooled}}}$$

$$= \frac{(0.0291 + 0.0136 + 0.0189)}{12 + 27 + 28}$$

$$= \frac{0.0825}{67}$$

$$= 0.0012$$

with 67 df. The estimated within-laboratory standard deviation is

$$\hat{\sigma} = \sqrt{\hat{\sigma}^2}$$

$$= \sqrt{0.0012}$$

$$= 0.035 \text{ gm/gm-mole.}$$

The laboratory term is significant for the second and third weeks of the test. The EMS for each of these terms is $\sigma^2 + 5\,\sigma_L^2$, and the two estimates of the laboratory bias variance are calculated as

$$\hat{\sigma}_{L_2}^2 = 0.0015$$

and

$$\hat{\sigma}^2_{L_2} = 0.0006.$$

Since both of these estimates have 6 df, the combined estimate is merely the average of the two, or

$$\hat{\sigma}^2_L = \frac{1}{2}(0.0015 + 0.0006)$$

$$= 0.0011$$

with 6 df. The estimated laboratory bias standard deviation, then, is

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}^2_L}$$

$$= \sqrt{0.0011}$$

$$= 0.033 \text{ gm/gm-mole}.$$

The between-laboratory term may be estimated from the above to be

$$\hat{\sigma}^2_b = \hat{\sigma}^2 + \hat{\sigma}^2_L$$

$$= 0.0012 + 0.0011$$

$$= 0.0023$$

with 6 df from the laboratory bias term. The estimated between-laboratory standard deviation is

$$\hat{\sigma}_b = \sqrt{0.0023}$$

$$= 0.048 \text{ gm/gm-mole}$$

B.7 Precision Estimation for Moisture Fraction Determination

The moisture fractions determined from the eight sampling trains are shown in Table 12. These are submitted to an ANOVA procedure according to the model

$$Y_{ij} = \mu + \rho_i + \tau_j + \epsilon_{ij}$$

where

μ – overall mean

ρ_i – effect due to run i

τ_j – effect due to train j

and

ϵ_{ij} – random error associated with Y_{ij}.

The model is a random effects model. The interaction between laboratories and runs is assumed to be zero, and the interaction term, then, is used as the error term in the analysis. This assumption is warranted, since the change in stack moisture content should have no effect on a laboratory's performance.

The ANOVA tables for each separate week are shown in Table B10. The EMS of the error term is σ^2, the within-laboratory variance. There are three estimates of σ^2, and these are pooled to give

TABLE B10. ANOVA FOR Bws DETERMINATION

Source	df	SS	MS	F	EMS
Week 1					
Runs	2	0.001406	0.000703	10.02*	
Trains	7	0.001822	0.000262	3.73*	$\sigma^2 + 3\sigma^2_L$
Error	14	0.000982	0.000070		σ^2
Total	23	0.004220			
Week 2					
Runs	4	0.001233	0.000308	3.57*	
Trains	7	0.000866	0.000123	1.43†	$\sigma^2 + 5\sigma^2_L$
Error	28	0.002417	0.000086		σ^2
Total	39	0.004516			
Week 3					
Runs	4	0.004782			
Trains	7	0.000240			
Error	28	0.001676			
Total	39	0.006698			

*Significant at 5% level.
†Insignificant.

$$\hat{\sigma}^2 = \frac{SS_{\text{pooled}}}{df_{\text{pooled}}}$$

$$= \frac{(0.000982 + 0.002417 + 0.001676)}{14 + 28 + 28}$$

$$= \frac{0.005075}{70}$$

$$= 0.000073$$

with 70 df. The estimated within-laboratory standard deviation is

$$\hat{\sigma} = \sqrt{0.000073}$$

$$= 0.009.$$

The trains term is significant only for the first week's data. The EMS of the trains component is $\sigma^2 + 3\sigma^2_L$. Solving for σ^2_L gives

$$\hat{\sigma}^2_L = \frac{MS_L - \hat{\sigma}^2}{3}$$

$$= 0.000064$$

with 7 df from the 8 trains. This gives an estimated laboratory bias standard deviation of

$$\hat{\sigma}_L = \sqrt{\hat{\sigma}^2_L}$$

$$= 0.008.$$

The between-laboratory variance is estimated from the above as

$$\hat{\sigma}^2_b = \hat{\sigma}^2 + \hat{\sigma}^2_L$$

$$= 0.000073 + 0.000064$$

$$= 0.000137.$$

The between-laboratory standard deviation is estimated to be

$$\hat{\sigma}_b = \sqrt{\hat{\sigma}^2_b}$$

$$= 0.012.$$

There are 7 df associated with this estimate, taken from the trains term.

B.8 Precision Estimation and Tests of Hypotheses for Particulate Concentration Corrected to 12% CO_2

The corrected particulate concentrations shown in Table 13 are submitted to statistical analysis according to the model in Appendix B.1. Each week's results are analyzed separately first, with 8 trains

(7 laboratories) per run. These ANOVA provide the estimates of the within-laboratory term, and the three tables generated are shown in Table B11.

TABLE B11. ANOVA FOR PARTICULATE CONCENTRATION CORRECTED TO 12% CO_2, INDIVIDUAL WEEKS

Source	df	SS	MS	F	EMS
Week 1 (Mean = 596.40)					
Runs	2	42,945.57	21,472.79	3.94*	–
Labs	7	134,463.36	19,209.05	3.53*	$\sigma^2 + 3\sigma^2_L$
Error	14	76,262.73	5,447.34		σ^2
Total	23	253,671.66			
Week 2 (Mean = 659.03)					
Runs	4	637,229.77	159,307.44	14.42*	–
Labs	7	1,006,676.51	143,810.93	13.01*	$\sigma^2 + 5\sigma^2_L$
Error	28	309,433.13	11,051.18		σ^2
Total	39	1,953,339.41			
Week 3 (Mean = 743.66)					
Runs	4	660,077.51	165,019.38	17.33*	
Labs	7	283,688.30	40,526.90	4.26*	
Error	27	257,054.05	9,520.52		
Total	38	1,200,819.86			
*Significant at 5% level.					

The differences between paired-laboratory trains was shown in Appendix B.2 to be insignificant, and the two concentrations in a given run were determined to be replicate Method 5 determinations. Using the formula in Appendix B.1, a pooled within-laboratory term can be estimated, as

$$s_p^2 = \sum_{i=1}^{13} \sum_{j=1}^{2} (Y_{ij} - \bar{Y}_{i\cdot})^2$$

for the 13 runs. Substituting the values from Table 13 into this formula gives

$$s_p^2 = 3072.88$$

with 13 df. This estimates σ^2, the within-laboratory variance. However, there is no effect in these results from the determination of CO_2 in the gas stream by Method 3.

A second estimate of σ^2 is obtainable directly from the ANOVA table. The EMS of the error term in the ANOVA tables is σ^2. Thus we have,

$$\hat{\sigma}_1^2 = 5447.34$$

$$\hat{\sigma}_2^2 = 11051.18$$

and

$$\hat{\sigma}_3^2 = 9520.52$$

from the three weeks. Using Bartlett's test, the three estimates above can be shown to be estimating the same true variance. The test statistic is $\chi^2 = 2.09$ with 2 df, and has a significance level of 0.35 associated with it. Thus the pooled estimate is used,

$$\hat{\sigma}^2 = 9315.22$$

with 69 df. This would give an estimated standard deviation of

$$\hat{\sigma} = 96.52$$

for the within-laboratory term.

The data from the 6 laboratories who participated in all 13 sampling runs are used to obtain the estimated laboratory bias component. The ANOVA table for the 3 week analysis is shown in Table B12. The laboratory term is significant, which allows contrasts among the means to be tested.

TABLE B12. ANOVA FOR PARTICULATE CONCENTRATION CORRECTED TO 12% CO_2, THREE-WEEK ANALYSIS

Source	df	SS	MS	F	EMS
Runs	12	1,152,948.09	96,079.01	5.80*	
Labs	5	771,566.39	154,313.28	9.31*	$\sigma^2 + 13\sigma_L^2$
4 vs 5	1	59,219.56	59,219.56	43.30*	
6 vs 7	1	11,779.33	11,779.33	38.76*	
8 vs 9	1	453,607.62	453,607.62	139.31*	
Error	59	977,989.77	16,576.10		σ^2
4 vs 5	12	16,410.11	1,367.51		
6 vs 7	12	3,646.97	303.91		
8 vs 9	12	39,072.88	3,256.07		
Total	76	2,902,504.25			

*Significant at 5% level.

The three contrasts between paired laboratories provide a total SS of 524,606.51, with 3 df. The mean square, then, is

$$MS_L = 524,606.51/3$$

$$= 174,868.84.$$

The EMS of this term is $\sigma^2 + 13\,\sigma_L^2$, so that

$$\hat{\sigma}_L^2 = \frac{MS_L - \hat{\sigma}^2}{13}$$

$$= \frac{174,868.84 - 3072.88}{13}$$

$$= 13,215.07$$

with 3 df. This gives an estimated standard deviation of

$$\hat{\sigma}_L = 114.96$$

for the laboratory bias term.

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